



TITLE:

Aptitude of pernambuco (*Guilandina echinata* Spreng.) as a violin bow and role of its extractives on the vibrational property(Dissertation_全文)

AUTHOR(S):

Matsunaga, Masahiro

CITATION:

Matsunaga, Masahiro. Aptitude of pernambuco (*Guilandina echinata* Spreng.) as a violin bow and role of its extractives on the vibrational property. 京都大学, 2000, 博士(農学)

ISSUE DATE:

2000-01-24

URL:

<https://doi.org/10.11501/3164166>

RIGHT:

**Aptitude of pernambuco (*Guilandina echinata* Spreng.) as
a violin bow and role of its extractives on the vibrational property**

MASAHIRO MATSUNAGA

1999

Contents

General Introduction	1
Chapter 1 Aptitude of Pernambuco as a Violin Bow	
1.1 Introduction	3
1.2 Materials and Methods	4
1.2.1 Materials	4
1.2.2 Measurement of the contents of extractives	7
1.2.3 Vibrational test	7
1.2.4 Dynamic viscoelastic test	9
1.2.5 Thermal softening test	9
1.2.6 Tests for the bending property and retention of the curvature	9
1.2.7 Shearing test	10
1.2.8 Indentation hardness test	10
1.3 Results and Discussion	10
1.3.1 Specific gravity	12
1.3.2 Content of extractives	12
1.3.3 Vibrational properties	15
1.3.4 Dynamic viscoelastic behaviors	17
1.3.5 Thermal softening	21
1.3.6 Easiness of bending and retention of the curvature	24
1.3.7 Shearing strength	27
1.3.8 Indentation hardness	30
1.4 Summary	33

Chapter 2 Effect of Extractives of Pernambuco on the Vibrational Properties

2.1 Introduction	34
2.2 Materials and Methods	35
2.2.1 Materials	35
2.2.2 Vibrational test after extraction with water	35
2.2.3 Color measurement	35
2.2.4 X-ray diffractometry	36
2.2.5 Analysis of water-soluble extractives of pernambuco	36
2.3 Results and Discussions	39
2.3.1 Change of vibrational properties after extraction with water	39
2.3.2 Relationship between wood color and properties	41
2.3.3 Mean microfibril angle	41
2.3.4 Analysis of water-soluble extractives of pernambuco	45
2.4 Summary	48

Chapter 3 Vibrational Property Changes of Spruce Wood by Impregnation with Extractives of Pernambuco

3.1 Introduction	49
3.2 Materials and Methods	49
3.2.1 Materials	49
3.2.2 Preparation of water-soluble extractives from pernambuco	50
3.2.3 Treatments of spruce wood with water-soluble extractives of pernambuco	50
3.2.4 Treatments of spruce wood with isolated extractives of pernambuco	51
3.2.5 Treatments of spruce wood with hematoxylin	51
3.2.6 Microscopic observation of filled specimens	52
3.3 Results and Discussion	52

3.3.1 Topological aspects of the extractives-treated specimens	52
3.3.2 Changes of vibrational properties	54
3.3.3 Influences of protosappanin B and hematoxylin on the vibrational properties	61
3.4 Summary	66

Chapter 4 Working Mechanism of Adsorbed Water on the Vibrational Properties of Wood Impregnated with Extractives of Pernambuco

4.1 Introduction	67
4.2 Materials and Methods	68
4.2.1 Preparation of water-soluble extractives from pernambuco	68
4.2.2 Preparation of moisture adsorption isotherms	68
4.2.3 Treatment of spruce wood with extractives	69
4.2.4 Measurement of frequency dependence of vibrational properties	69
4.2.5 Measurement of temperature dependence of $\tan \delta$	69
4.3 Results and Discussion	71
4.3.1 Analysis of adsorption isotherm	71
4.3.2 Frequency dependence of vibrational properties	73
4.3.3 Temperature dependence of $\tan \delta$	81
4.4 Summary	88

Conclusions

Acknowledgements

References

General Introduction

Wood has been utilized as various materials, such as construction materials, furniture, applied arts and so on, because of its easy processing, fine appearance, high strength irrespective of low density. However, properties of wood are different among various wood species. For example, it is generally said that Japanese cypress (*Chamaecyparis obtusa* Endl.) is suited to a material of wooden house because of its durability, weather-proof property, decay resistance, termite resistance and easy processing. It is also commonly known that royal paulownia (*Paulownia tomentosa* Steud.) is suitable for a materials of chest of drawers by reason of its high dimensional stability, moisture-proof property, easy shaving and processing as well as fine appearance.

Wood is an indispensable material for musical instruments. Special wood species have been traditionally used for musical instrument. For the almost all of the musical instrument, the suitability may be closely related to the acoustic property. For instance, Sitka spruce (*Picea sitchensis* Carr.) is usually used for the soundboard of piano and violin because of its high Young's modulus in spite of low density and low loss tangent (Fukada 1951, Meinel 1957, Norimoto 1982). On the other hand, some wood species are used for special use, but the suitability have not been proved well.

The heartwood of pernambuco (*Guilandina echinata* Spreng. syn *Caesalpinia echinata* Lam.), which is a kind of Brazilian hardwood, has been used as the materials for the excellent bow for playing stringed instruments for a long time. This wood species is classified into a diffuse-porous wood, and the heartwood is yellowish to reddish. It is known that pernambuco was brought to Europe because its extractives were available as a dyestuff, and that it began to be used as bows of stringed instruments (Imaizumi 1992). However, there is no report to describe

scientifically why pernambuco is suitable for the bow. This wood species may be selected based on the experiences of bow makers and violin players during many years.

Pernambuco has been cut down to date, and the production of good quality timber is decreasing from year to year. Moreover, the yield for bows is fairly low because of a lot of knots and other defects such as distortion. Thus, nowadays, alternative wood species are being searched and tested as the bow materials instead of pernambuco. However, the bows made from these wood species are not highly evaluated.

In Chapters 1 and 2 of this thesis, the physical and mechanical properties of pernambuco, substitutable wood species and many common hard wood species were widely investigated. From a comparative study of the characteristics of the pernambuco and other species, the properties required for bow material were explored. During the execution of this study, it was found that a certain vibrational property of pernambuco was quite different from other many wood species examined. It was also supposed that the peculiar vibrational property is attributed to the large amount of extractive components in pernambuco. In Chapter 3, then, the extractives of pernambuco were impregnated into the other wood species, and the influence of this treatment on the vibrational properties was examined. In Chapter 4, the mechanism of the changing vibrational properties due to impregnation with extractives was comprehensively discussed in relation to the adsorbed water.

Chapter 1 Aptitude of Pernambuco as a Violin Bow

1.1 Introduction

The heartwood of pernambuco (*Guilandina echinata* Spreng. syn *Caesalpinia echinata* Lam.), a Brazilian hardwood, has been used to make violin bows for more than 200 years. However, the reason why pernambuco is suitable for bows has not been clarified. Nowadays, the lack of pernambuco resources is serious, and recently the deforestation of pernambuco was prohibited. Though the violin bow is also made from the other wood species, the alternative wood species whose property is comparable to that of pernambuco has not been found yet. If the necessary conditions required for violin bow is clarified, it would be convenient to search the substitutable wood for pernambuco, and would become possible to imitate the wood property to that of pernambuco by the chemical and/or physical processings.

The suitability of the wood material for musical instruments is commonly related with the vibrational property. Generally, wood with high specific dynamic Young's modulus (E'/γ : where E' is dynamic Young's modulus and γ is specific gravity) and low loss tangent ($\tan \delta$) is accepted to be suitable for the soundboards of musical instruments. This means that the lower the energy loss due to the viscosity is, in other words, the higher the converting efficiency of a given energy to the kinetic energy is, the more suited the material is for soundboards. Tanaka *et al.* (1987) reported that the efficiency which vibrational energy is converted into sonic energy, that is, acoustic converting efficiency (ACE), is proportional to $\sqrt{(E'/\gamma^3)} / \tan \delta$. Therefore, E'/γ and $\tan \delta$ are two main factors which affect the ACE. In the soundboard of pianos, guitars, and violins, for example, it has been reported that the wood material rated highest by the skillful musical instrument maker showed extremely high E'/γ and low $\tan \delta$ values (Norimoto 1982, Yano

et al. 1990, 1992). Though the violin's bow itself does not produce sound, E'/γ and $\tan \delta$ would be meaningful indicators for evaluating the quality as a bow.

The ease of handling during the manufacturing process and endurance of performance under use as well as the vibrational property seem to be important for the material of a bow. For example, a curvature, which offers tensile force to the horse hair (Fig. 1-1), is created in the bow by heating. Thus the ease of handling and permanent retention of this deformation may also be required. The top part of the bow (called the "head", Fig. 1-1) is easy to break along a longitudinal direction when it is carelessly handled, so the strength of the head is another important factor.

In this chapter, the physical and mechanical properties of pernambuco, substitutable wood species and many common hardwoods were widely measured. From a comparative study of the characteristics of the pernambuco and other species, the properties required for a bow material were explored.

1.2 Materials and Methods

1.2.1 Materials

Specimens were cut from heartwoods of the following five wood species:

1. Pernambuco (*Guilandina echinata* Spreng.)

Family: Leguminosae

Growing district: Brazil

Color: yellowish to reddish

This wood has been used as the materials for the excellent bow.

2. Massaranduba (*Manilkara bidentata* A. Chev.)

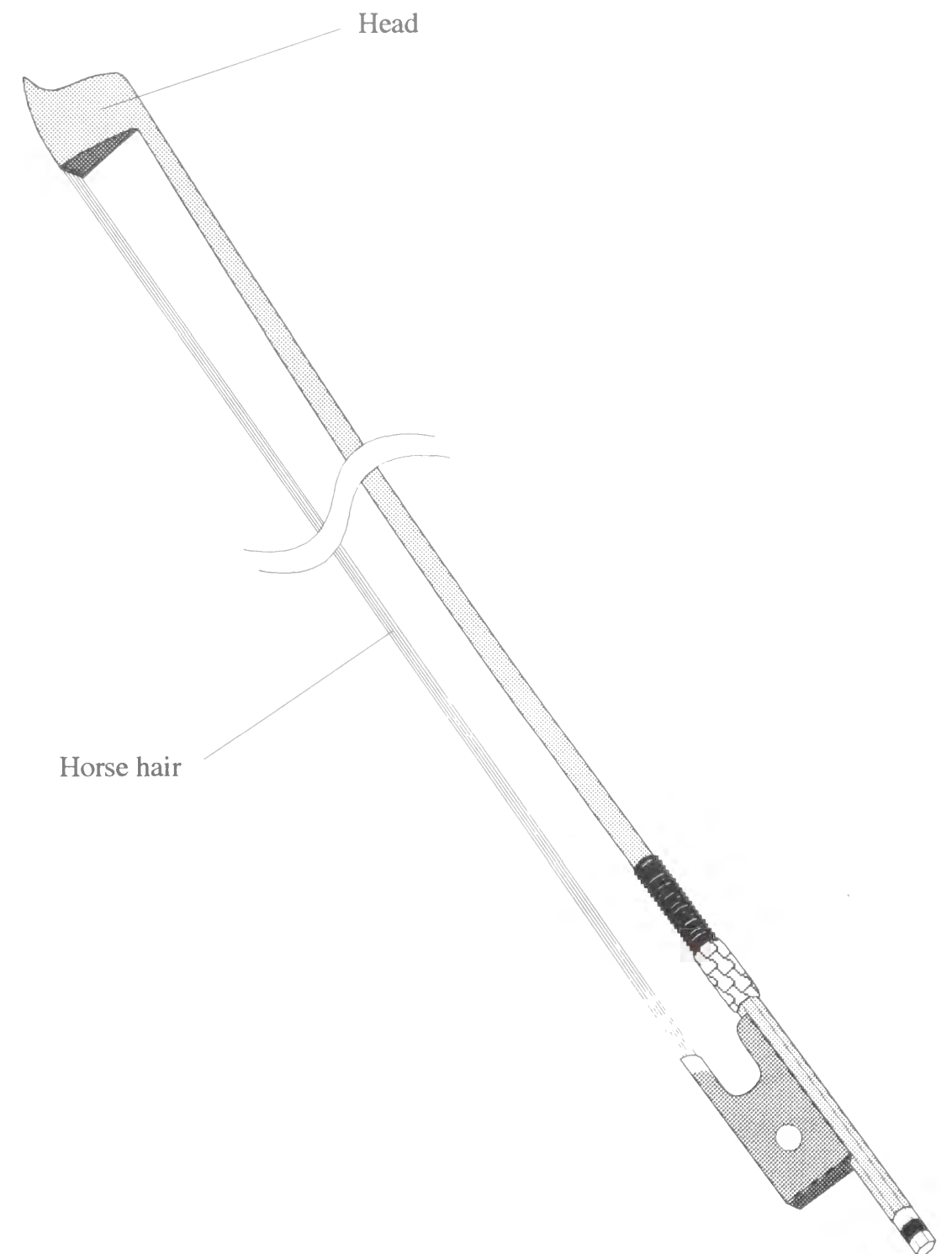


Fig. 1-1. Scheme of violin bow.

Family: Sapotaceae

Growing district: Brazil

Color: Light to dark reddish brown

This wood has been sometimes used as a bow.

3. Kerandji (*Dialium* spp.)

Family: Leguminosae

Growing district: Malaysia, Indonesia

Color: Light to yellow brown

Bows made of this species are evaluated to be comparable to those of pernambuco, and are experimentally on sale.

4. Pao rosa (*Swartzia fistuloides* Harms)

Family: Leguminosae

Growing district: West Africa

Color: Dark red to rose red

This species is under investigation for bow use.

5. Blackbutt (*Eucalyptus pilularis* Sm.)

Family: Myrtaceae

Growing district: Australia

Color: Whitish or pale brown

This is abundantly yielded, but has not been effectively used yet.

The test specimens of pernambuco, massaranduba, and kerandji were cut from a lot of bar-shaped materials, which were rejected for bow processing because of their partial defects. The specimens of pao rosa and blackbutt were prepared from

several pieces of board-shaped or bar-shaped timbers. A piece of specimen for the respective wood species was subjected to the determination of dynamic viscoelastic properties, and the numbers of the specimens for the other tests are shown in Tables 1-2, 1-3, 1-4, 1-5 and 1-6 (see below). The specific gravity in oven-dry was measured for the specimens for vibrational, shearing and hardness tests after drying at 60 °C under vacuum for two days. Furthermore, 19 kinds of Brazilian hardwood and 13 kinds of Japanese hardwood were also subjected to the vibrational property test (Table 1-1). Five pieces of specimens were used for irrespective wood species.

1.2.2 Measurement of the contents of extractives

Pernambuco and four species of substitutable wood were ground with a Wiley mill to pass through a sieve with 355 μ m apertures but not one with 150 μ m. The wood meal of pernambuco was classified into three groups depending on the depth of color.

One part of the wood meal (2 g) was subjected to the determination of the hot water extractives. The weighed wood meal was boiled in water (100 ml) under reflux for 3 hours and filtrated through a glass filter (G 3). The residue was rinsed with hot water, dried at 105 °C, and weighed.

The other part of the wood meal (2 g) was extracted with ethanol/benzene (v/v=1:2, 170 ml) for 6 hours using a Soxhlet's extractor.

1.2.3 Vibrational test

Specimens of 100 to 150 mm (longitudinal direction, L) \times 10 to 12 mm (radial direction, R) \times 2 mm (tangential direction, T) were used. Vibrational properties were measured by a free-free flexural vibration method (Hearmon 1966). The E'/γ in the longitudinal direction was calculated from the resonant frequency of the first vibrational mode using the Euler-Bernoulli equation

Table 1-1. Wood species tested.

Common names	Family names	Botanical names
Balata	Sapotaceae	<i>Manilkara bidentata</i> A. Chev.
Copaiba	Leguminosae	<i>Copaifera langsdorffii</i> Desf.
Copal	Caesalpinaceae	<i>Hymenaea courbaril</i> L.
Cordia wood	Borraginaceae	<i>Cordia alliodora</i> Oken.
Cumarú	Leguminales papilionaceae	<i>Dipteryx odorata</i> Willd.
Cupruba	Celastraceae	<i>Goupia glabra</i> Aubl.
Faveiro	Leguminosae mimosaceae	<i>Pterodon pubescens</i> Benth.
Ipe	Bignoniaceae	<i>Tecoma impetiginosa</i> Mart.
Jarana	Lecythidaceae	<i>Holopyxidium jarana</i> (Huber) Ducke
Jatoba	Leguminosae	<i>Hymenaea</i> sp.
Marupa	Simaroubaceae	<i>Simaruba amara</i> Ajbl.
Piquia	Caryocaraceae	<i>Caryocar villosum</i> Pers.
Piquia rana	Caryocaraceae	<i>Caryocar costarricense</i> Conn. Sm. yC
Red Louro	Lauraceae	<i>Ocotea rubra</i> Mez.
Sapucaia	Lecythidaceae	<i>Letythis</i> sp.
Satinwood	Moraceae	<i>Brosimum</i> sp.
Sucupira	Leguminosae	<i>Bowdichia</i> sp.
Tache	Leguminosae	<i>Myroxylon balsamum</i> Harms
Tatajuba	Moraceae	<i>Chlorophora tinctoria</i> Gaud.
Kaede	Aceraceae	<i>Acer</i> sp.
Kashi	Fagaceae	<i>Quercus</i> sp.
Kusu	Lauraceae	<i>Cinnamomum camphora</i> (L.) Sieb.
Kuri	Fagaceae	<i>Castanea crenata</i> S. and Z.
Keyaki	Ulmaceae	<i>Zelkova serrata</i> Makino.
Konara	Fagaceae	<i>Quercus serrata</i> Thunb.
Sakura	Rosaceae	<i>Prunus</i> sp.
Shinoki	Fagaceae	<i>Shiina sieboldi</i> L.
Shide	Betulaceae	<i>Carpinus</i> sp.
Tochinoki	Hippocastanaceae	<i>Aesculus turbinata</i> Bl.
Buna	Fagaceae	<i>Fagus crenata</i> Bl.
Mizunara	Fagaceae	<i>Quercus mongolica</i> Fisch var. <i>grosseserrata</i> Rehd. et Wils.
Mizume	Betulaceae	<i>Betula grossa</i> S. and Z.

(Kitahara 1966), and the $\tan \delta$ from the decremental curve of the vibration at the resonant frequency. The frequency range of measurement was about 300 to 1200 Hz. The measurements were carried out in a chamber maintained at 20 °C and 65% relative humidity (R.H.).

1.2.4 Dynamic viscoelastic test

Specimens of 70 mm (L) \times 4 mm (R) \times 1 mm (T) were used. Dynamic Young's modulus (E'), dynamic loss modulus (E'') and $\tan \delta (= E'' / E')$ were measured by a forced vibrational method, where a dynamic viscoelastic measuring apparatus (Orientec Co., LTD. Reovibron DDV-25PF) was used. The specimens were subjected to a vibration of 11 Hz under 7.84 N of tension. The temperature range and increasing rate of the temperature were from -150 to 300 °C and 1 °C/min, respectively. The span length was 55 mm. The specimens were measured in an oven-dried state.

1.2.5 Thermal softening test

The wood meals were prepared by the method described in 1.2.2. Half of the wood meal was extracted with ethanol/benzene (v/v = 1:2) for 6 hours by a Soxhlet's extractor. Both the extracted and unextracted wood meals were used for the thermal softening test. The wood meal was stuffed into a glass tube (2 mm in diameter). The height of the stuffed wood meal was about 10 mm. The change of the height during heating was measured as the volumetric change through a differential transformer. The temperature range and increasing rate of temperature change were from 50 to 300 °C and 2 °C/min, respectively.

1.2.6 Tests for the bending property and retention of the curvature

A specimen measuring 150 mm (L) \times 12 mm (R) \times 2 mm (T) was heated at

280 °C for 90 sec in an oven, placed between curved steel plates (curvature 6.61), and fixed by bolts (Fig. 1-2(a)). The whole device was cooled under atmospheric conditions. Ten minutes later the steel plates were removed, and the curvature of the specimen was measured. The specimens were then placed in a desiccator maintained at 20 °C and 66% R.H. After 2 weeks the specimen was held between flat steel plates and pinched by clips (Fig. 1-2(b)), and then the change of the curvature that occurred with the passage of time was measured.

1.2.7 Shearing test

Specimens of 35 mm (L) × 20 mm (R) × 10 mm (T), which had a notch of 10 mm (L) × 10 mm (R) × 10 mm (T) were used. The specimens were sheared parallel to the tangential plane by means of a compression test apparatus (Mori Shikenki Seisakusho Inc.), and the maximum load was measured in accordance with JIS 2101. The shearing rate was about 1 mm/min. Shearing strength was calculated by dividing the maximum load by the shearing area. The tests were carried out in a surrounding atmosphere at April.

1.2.8 Indentation hardness test

The specimens of 157 mm (L) × 10 mm (R) × 10 mm (T) were subjected to the test. Using a hardness measuring apparatus (Tokyo Koki Seizosho), a steel ball (10 mm in diameter) was pressed into the radial and tangential faces of the specimen in accordance with JIS 2101. The force needed to press the steel ball until $1/\pi \div 0.32$ mm in depth was measured. The pressed surface area is 10 mm². The pressure per pressed surface area was defined as indentation hardness. The measurements were carried out in a surrounding atmosphere at May.

1.3 Results and Discussion

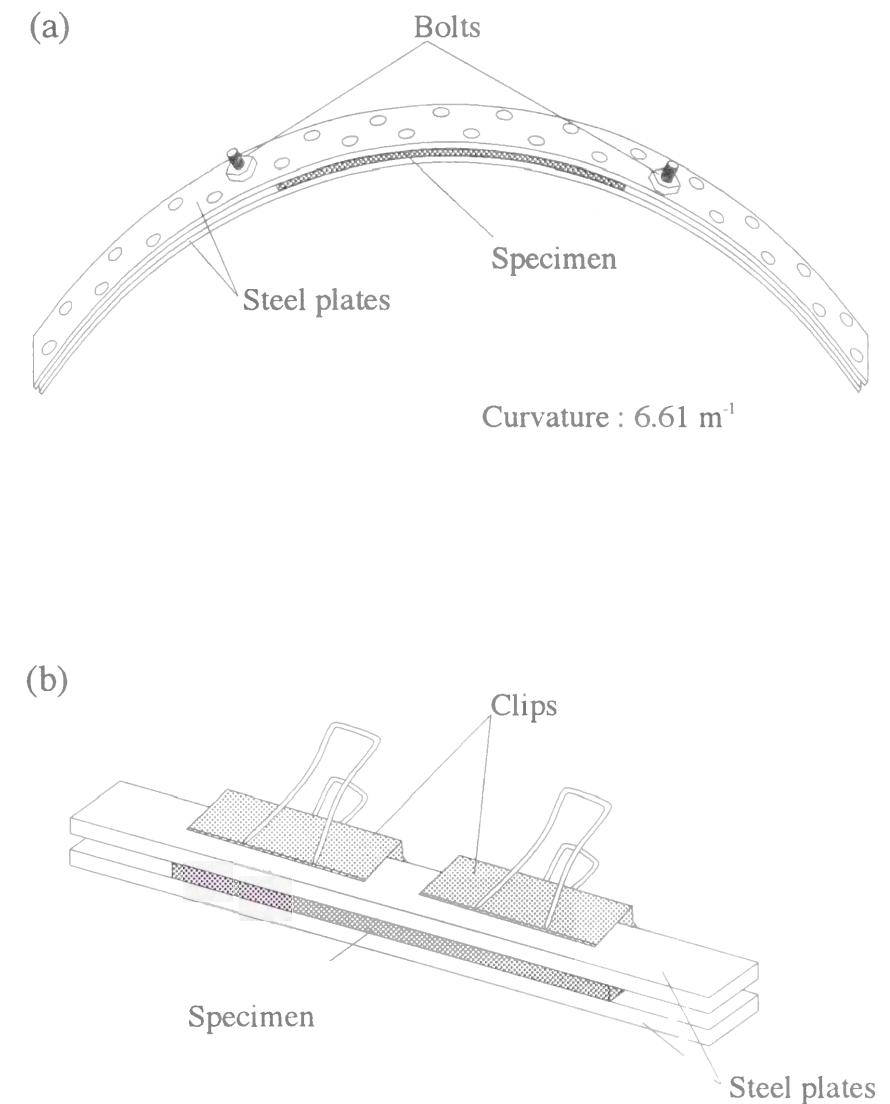


Fig. 1-2. Devices for fixation (a) and forced recovery (b) of the curvature.

1.3.1 Specific gravity

The mean values and standard deviations of the specific gravity in oven-dry are shown in Table 1-2 for the specimens subjected to the vibrational test. The mean values were above 0.9 except for blackbutt. However, the specific gravities of blackbutt distributed so widely that many specimens had a specific gravity which was as high as other wood species. The specific gravities in oven-dry of pernambuco also distributed widely (Fig. 1-3).

1.3.2 Content of extractives

The content of extractives is summarized in Table 1-3 for each wood species. Pernambuco had the highest content of the hot water extractives, and the darker fraction of pernambuco showed higher extractives content. However, total extractives content of pernambuco may be higher because the coloration of the water did not completely cease even after many times of repeating extractions. Pao rosa had the highest content of the ethanol-benzene extractives, which was more than twice as that of pernambuco.

Table 1-3. Extractives contents for each species.

	Hot water (%)	Ethanol-benzene (%)
Pernambuco (light)	12.6	7.8
Pernambuco (medium)	13.0	9.2
Pernambuco (dark)	15.7	8.7
Massaranduba	6.5	4.2
Kerandji	7.3	5.4
Pao rosa	10.2	21.2
Blackbutt	6.0	1.7

Table 1-2. Properties of the specimens subjected to the vibrational test.

Number	Specific gravity in oven-dry		E'/γ (GPa)		$\tan \delta$	
	m.v.	s.d.	m.v.	s.d.	m.v.	s.d.
Pernambuco	100					
	0.920	0.067	19.8	3.7	4.12×10^{-3}	1.04×10^{-3}
Massaranduba	69		15.7	1.8	10.04	1.17
Kerandji	18		24.6	2.3	5.74	0.50
Pao rosa	16		13.9	1.0	7.41	0.64
Blackbutt	43		28.7	3.0	6.20	0.61

m.v.: mean value, s.d.: standard deviation.

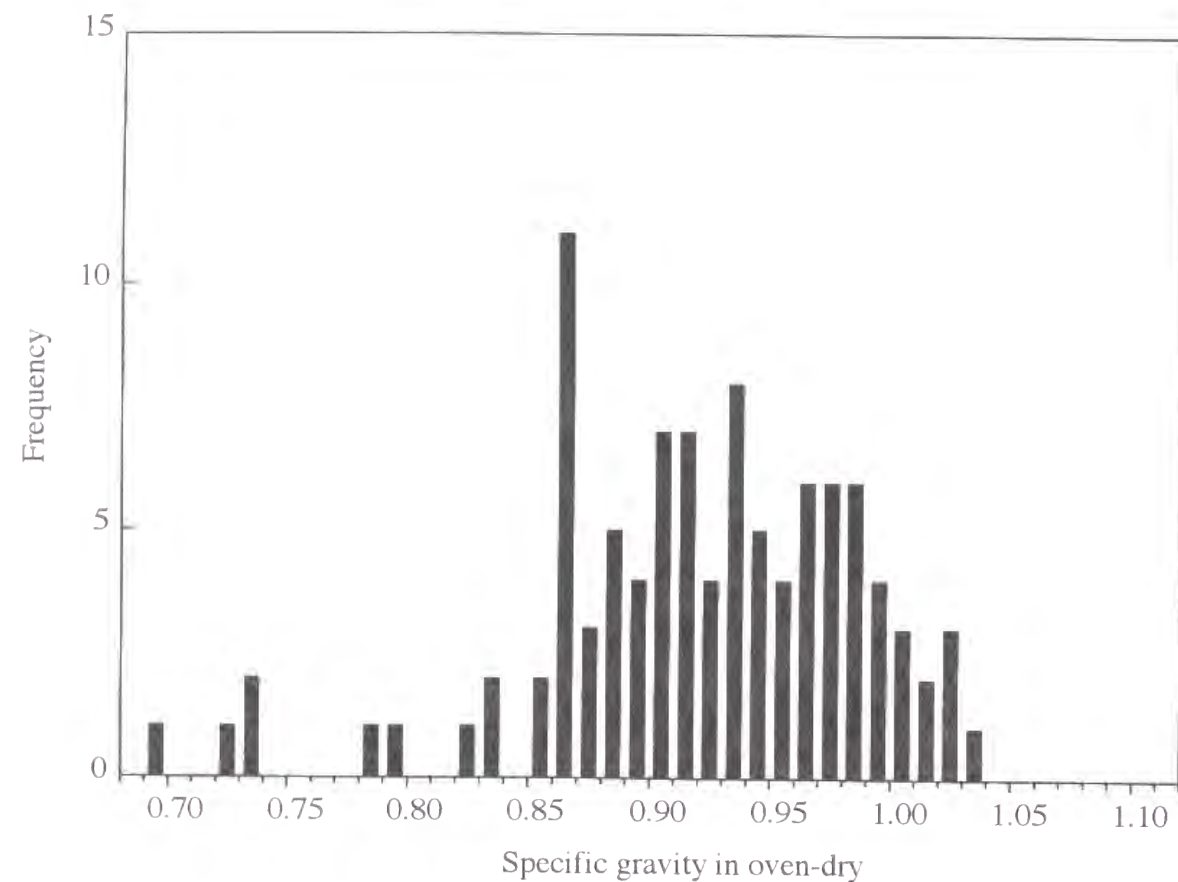


Fig. 1-3. Histogram of specific gravity in oven-dry of pernambuco

1.3.3 Vibrational properties

The mean values of E'/γ ranged from 13.9 GPa for pao rosa to 28.7 GPa for blackbutt. Pernambuco showed intermediate value (about 20 GPa) among five wood species. However, the large standard deviations of pernambuco and blackbutt show that their individual Young's moduli are widely scattered. The values of E'/γ were plotted against specific gravity in oven-dry for each specimen in Fig. 1-4(a). The plots for pernambuco and blackbutt were distributed more widely than those for the other species. Figure 1-4(b) shows the relationship between the mean values of specific gravity in oven-dry and E'/γ for pernambuco, 19 kinds of Brazilian hardwood and 13 kinds of Japanese hardwood. It was found that pernambuco has relatively high specific gravity and ordinary value of E'/γ among common hardwoods.

It is commonly known that the weight and length of a violin bow are about 60 g and 73 cm, respectively (Imaizumi 1992). Therefore, it is difficult to make uniform bows from pernambuco because of the wide distributions of specific gravity and Young's modulus. High flexural rigidity is required to endure the tension of horse hair, but thickening the bow for this purpose will be ugly (generally, slender bow tends to be preferable) and too heavy. Accordingly, the lower limit of Young's modulus needed for the bow must exist, but the ultimate Young's modulus can't be declared for the present. However, judging from the fact that the bow shape has been unchanged since pernambuco was used for bow for the first time in the latter half of the 18th century (Imaizumi 1992), and that the mean value of Young's modulus of pernambuco is not always characteristic among many wood species (Fig. 1-4(b)), the shape of bow seems to be necessarily decided from the mean values of specific gravity and Young's modulus of pernambuco.

The mean values of $\tan \delta$ also differed widely from one species to another. In

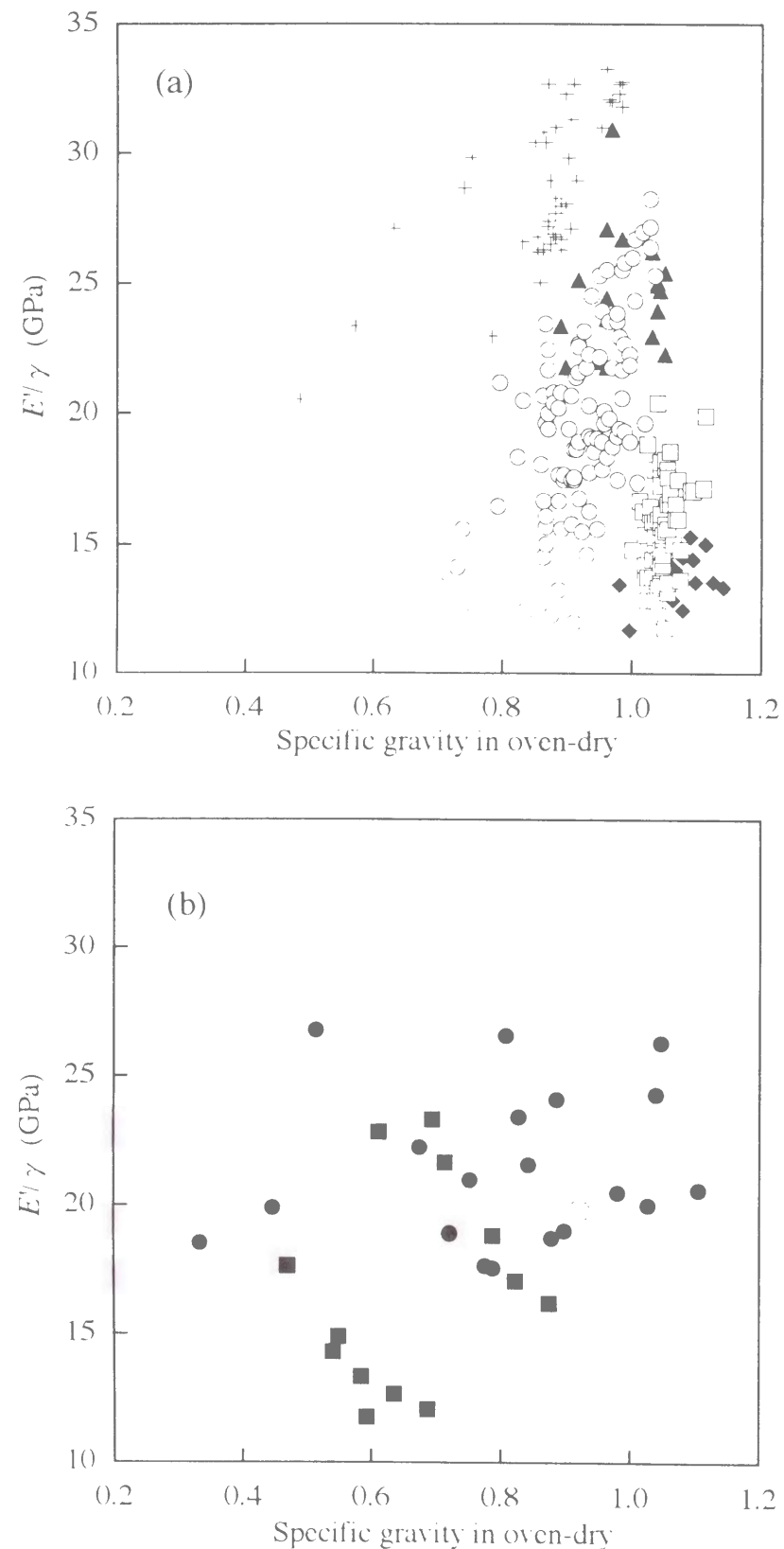


Fig. 1-4. Relationship between specific gravity in oven-dry and E'/γ .
 (a); Pernambuco and other substitutable wood species, (b);
 Average values for pernambuco and common hardwoods.
 ○; Pernambuco, ○; Massaranduba, ▲; Kerandji, ◆; Pao rosa,
 ○; Blackbutt, ●; Brazilian hardwood, ■; Japanese hardwood.

the case of pernambuco, the $\tan \delta$ was characteristically lower (0.00412) than any other substitutable wood species (Table 1-2), however, standard deviation of $\tan \delta$ was not so great as that of specific gravity or Young's modulus. Relationship between E'/γ and $\tan \delta$ is shown in Fig. 1-5. This figure clearly shows the peculiarity of $\tan \delta$ for pernambuco. In Fig. 1-5(a), the plots for each wood species fell down on a respective straight line, but the plots for pernambuco had a gentle slope and was located in the lower $\tan \delta$ region. From Fig. 1-5(b), it is apparent that the $\tan \delta$ of pernambuco is exceptionally low compared with many common hardwoods. Figure 1-6 shows the relationship between specific gravity in oven-dry and $\tan \delta$. Pernambuco has lower $\tan \delta$ than the other wood species irrespective of specific gravity.

The value of $\tan \delta$ is a measure of the vibrational decrement. A bow with a low $\tan \delta$ absorbs less vibrational energy itself when string is rubbed. In other words, the vibrational energy is effectively transferred to the string. Moreover, low vibrational decrement agrees with the demand of the violin player to feel the friction of the horse hair with the string. Thus, low $\tan \delta$ is also an important factor for bow handling. Consequently, pernambuco with constant low is highly appraised for bow material.

1.3.4 Dynamic viscoelastic behaviors

In the manufacturing of bow, the stick is heated in a flame at considerably elevated temperature to yield the curvature. Consequently, it is necessary to clarify the easiness of bending in the flame. Therefore, the temperature dependencies of E'/γ and $\tan \delta$, which are important factors for the wood substance for musical instruments, were measured in a wide temperature range.

The temperature dependencies of E' for each wood species are shown in Fig. 1-7. The values of E' of all wood species decreased gradually with an increase of

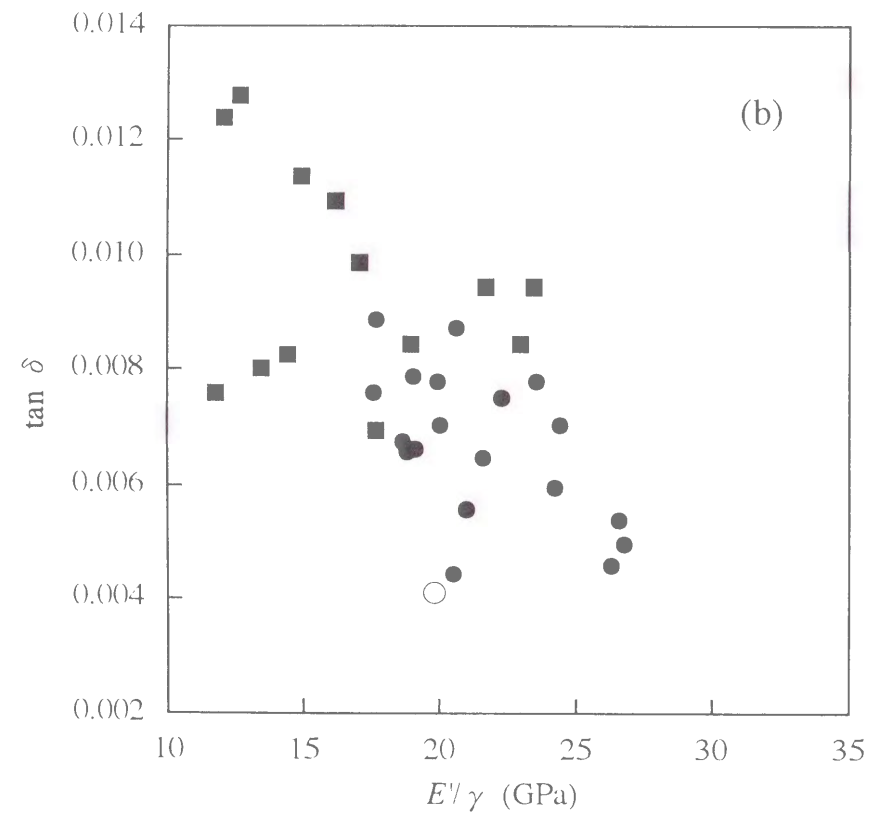
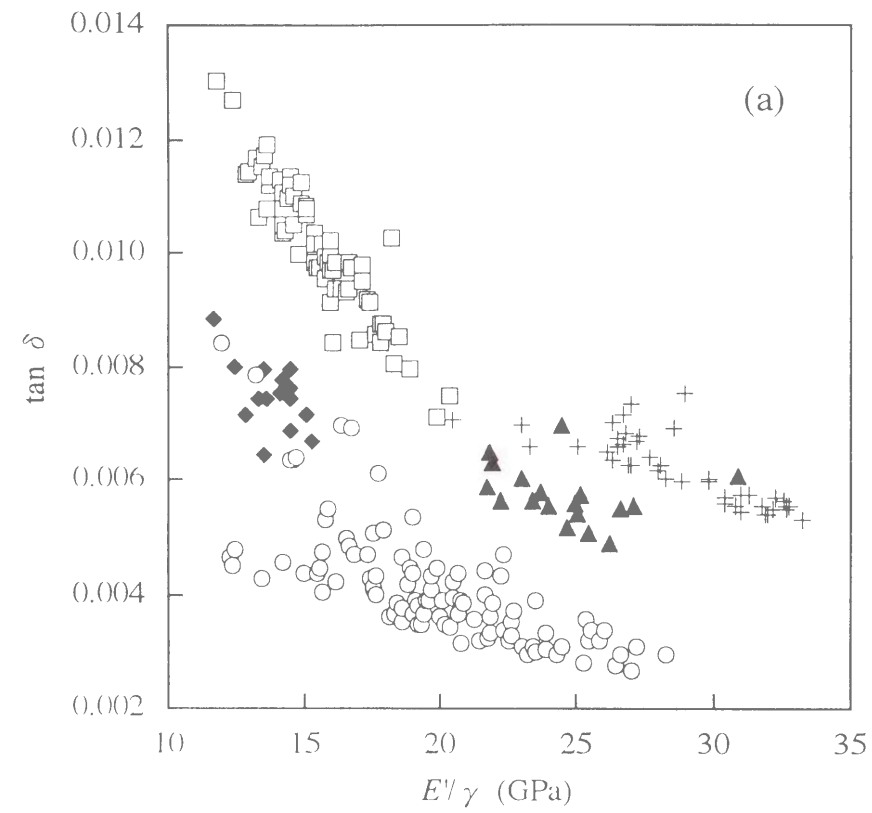


Fig. 1-5. Relationship between $E'\gamma$ and $\tan \delta$. (a); Pernambuco and other substitutable woodspecies, (b); Average values for pernambuco and common hardwoods. Legends are the same as in Fig. 1-4.

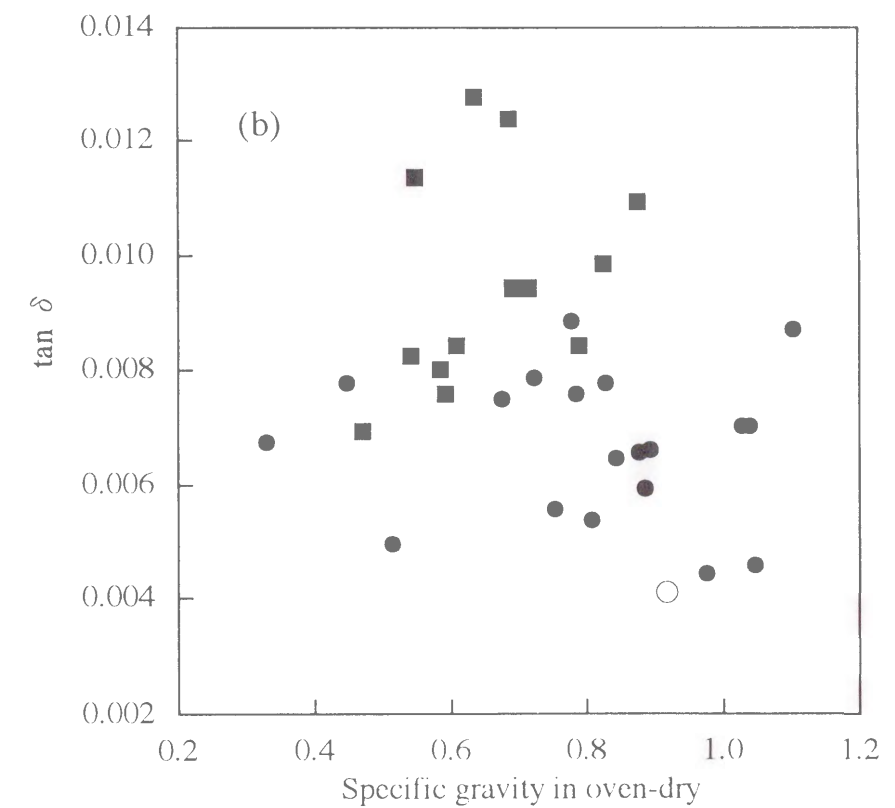
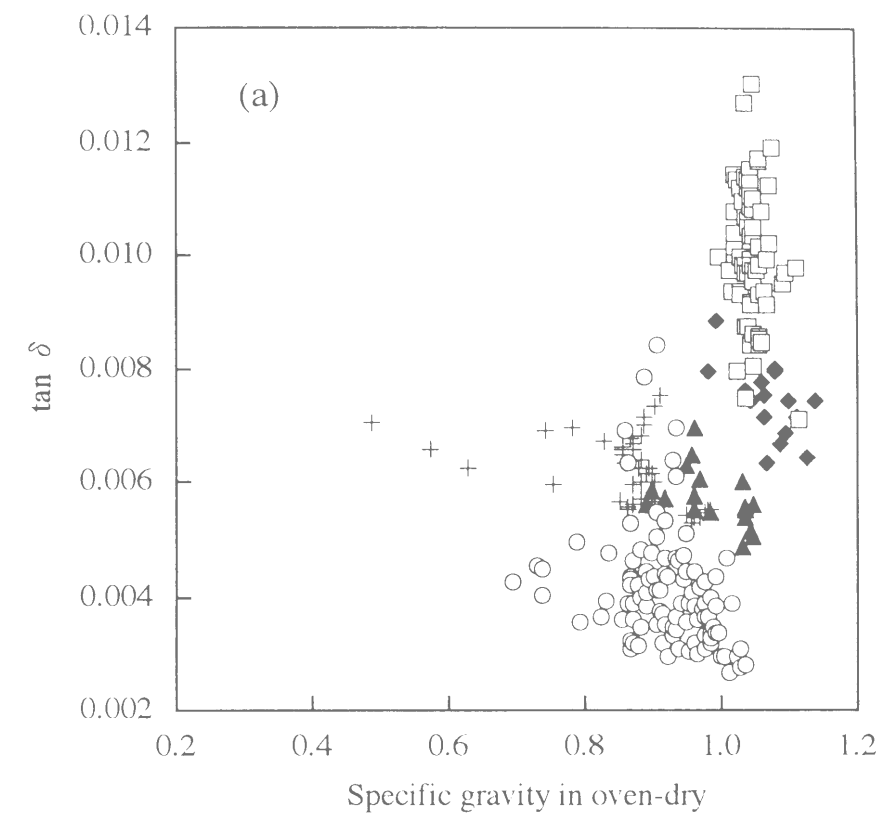


Fig. 1-6. Relationship between specific gravity in oven-dry and $\tan \delta$. (a); Pernambuco and other substitutable wood species, (b); Average values for pernambuco and common hardwoods. Legends are the same as in Fig. 1-4.

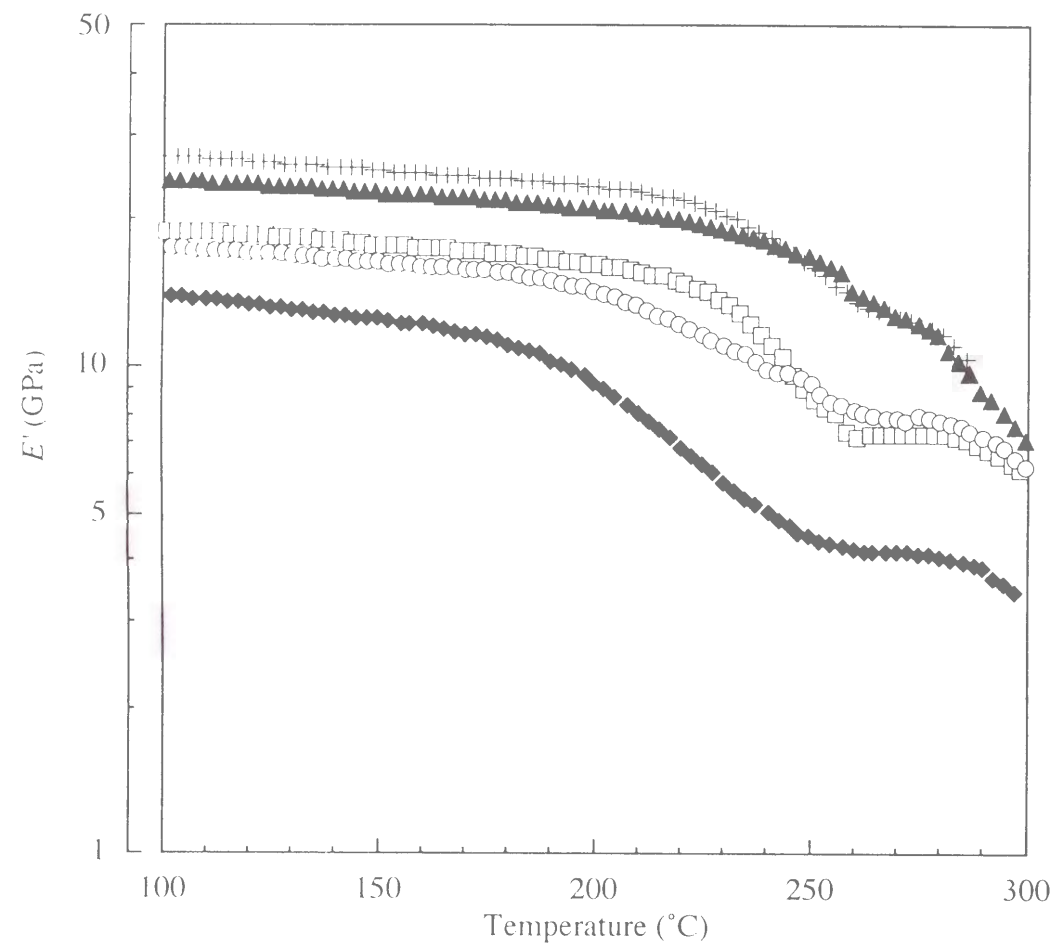


Fig. 1-7. Temperature dependencies of E' . Legends are the same as in Fig. 1-4.

temperature up to 150 °C, and above about 200 °C it fell steeply. Figure 1-8 shows the dependencies of E'' which corresponds to the changing rate of E' . Large peaks called primary dispersion (or α dispersion) are observed between 200 and 300 °C. Above this temperature, the micro Brownian movement of polymer chain becomes excited and the polymer loses resistance against external forces. In other words, the temperature range at which the E'' becomes maximum is the softening temperature. The maximum E'' of pernambuco and pao rosa appeared at a lower temperature than the other wood species (Fig. 1-8). It is also found that the wood with a higher content of extractives showed the peak at lower temperature. Narayanamurti (1957) reported that some extractives act as plasticizers at high temperatures to soften the cell wall. Therefore, the decrease of Young's modulus at high temperature is probably due to the softening of extractives, which may restrain the free movement of cellulose chain. However, because the components of extractives are not the same in each wood species, it cannot be explained that the softening temperature is dependent only upon the content of extractives. Nevertheless, the existence of extractives has presumably some effect on the retention of the form as well as thermal bending processing.

The temperature dependencies of $\tan \delta$ are shown in Fig. 1-9. The $\tan \delta$ of pernambuco was not always low during the whole temperature range, but was low only at around room temperature at which the bow is used. The $\tan \delta$ values of pernambuco and pao rosa began to increase at lower temperatures than those of massaranduba, kerandji and blackbutt. It is probable that $\tan \delta$ is also closely related to the content of extractives.

1.3.5 Thermal softening

It was found that pernambuco and pao rosa, which contain large amounts of extractives, showed lower softening temperature than the other wood species. This

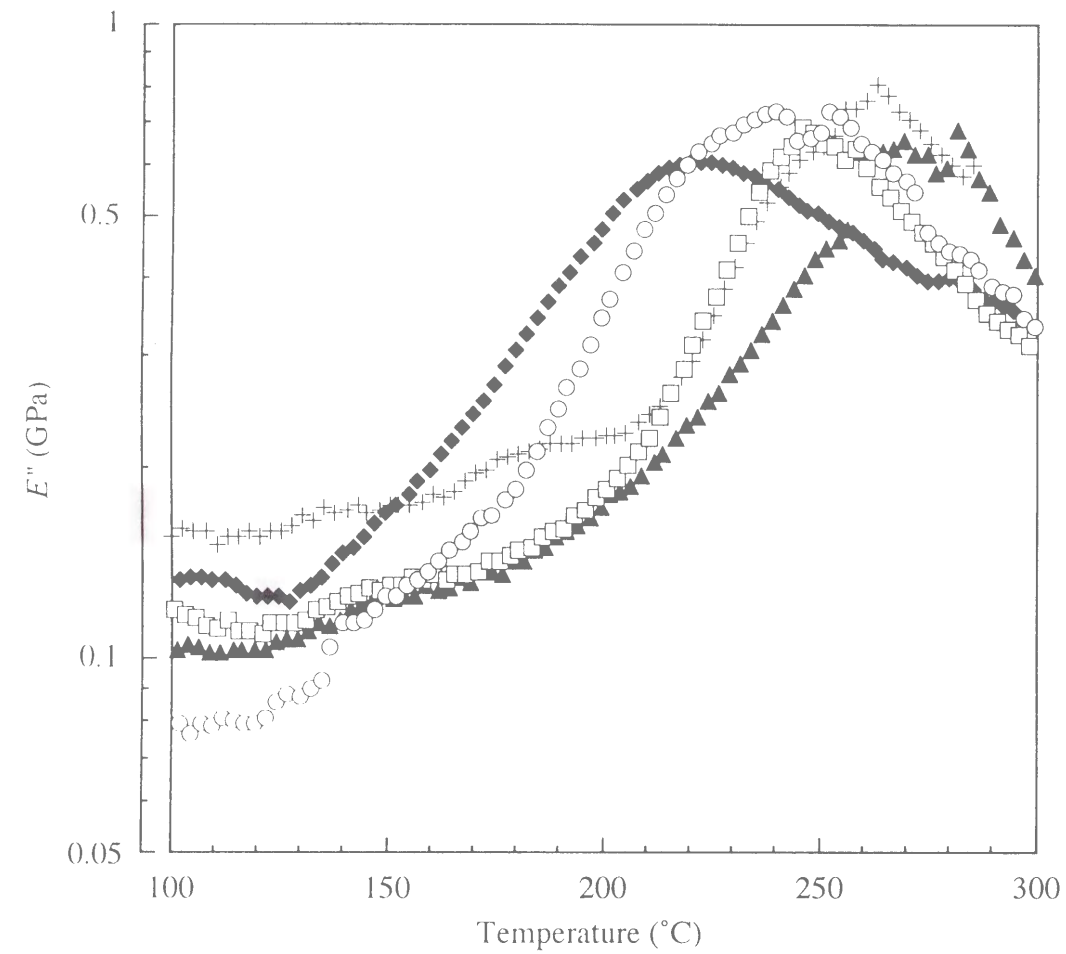


Fig. 1-8. Temperature dependencies of E'' . Legends are the same as in Fig. 1-4.

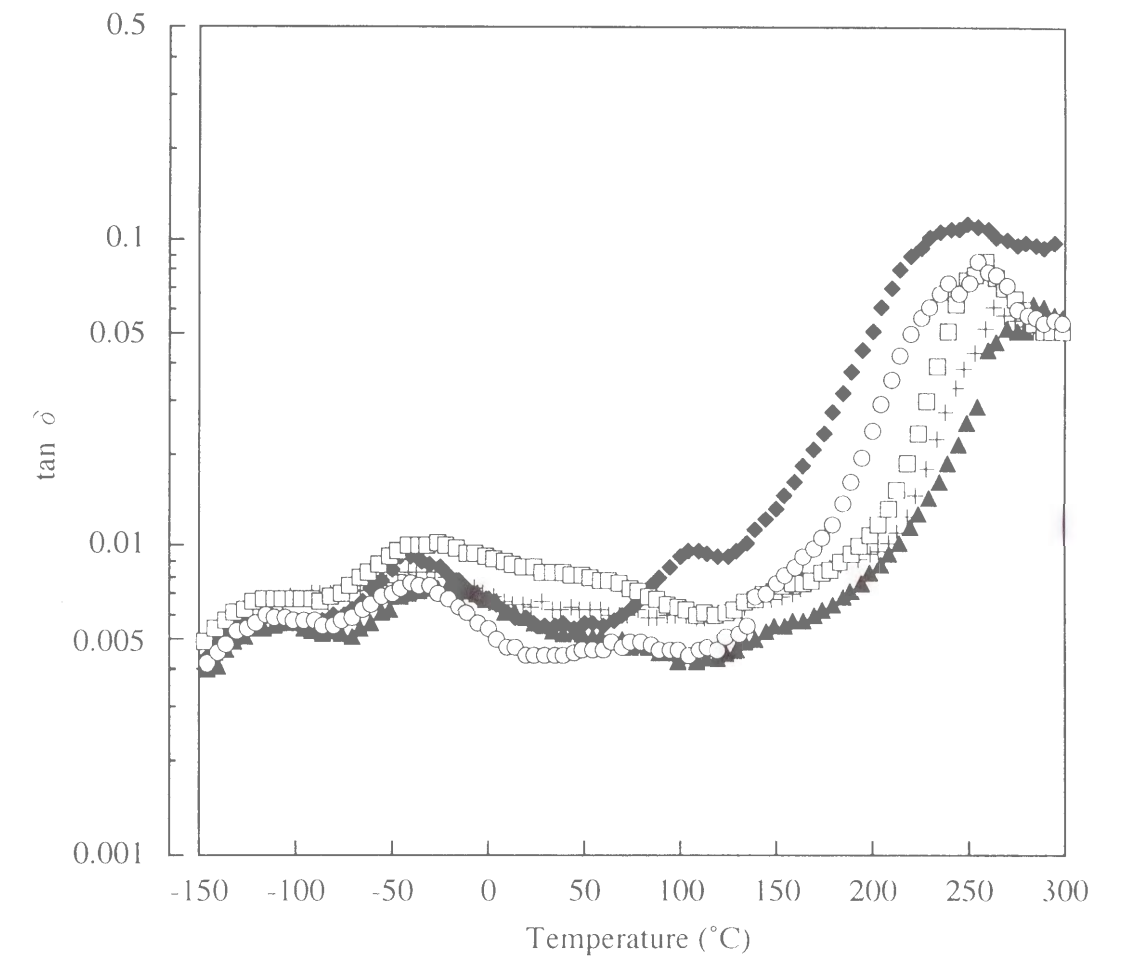


Fig. 1-9. Temperature dependencies of $\tan \delta$. Legends are the same as in Fig. 1-4.

finding suggests that extractives affect the softening temperature of wood. Thus the thermal softening of extracted and unextracted wood meal were measured, and the relationship between the softening temperature and the extractives content was examined.

The results are shown in Fig. 1-10. For unextracted wood meals of all wood species, significant decreases of volume were observed between 150 and 200 °C. Pao rosa, which has a large amount of the ethanol-benzene extractives, especially showed a marked change. On the other hand, the volume changes in extracted wood meals were only slight, irrespective of the wood species. These results support author's proposal that the decrease of dynamic Young's modulus above 200 °C (Fig. 1-7) may be attributed to the softening of extractives which restrain the free movement of the cellulose chain.

1.3.6 Easiness of bending and retention of the curvature

As mentioned above, it is found that the extractives affect the softening of wood material. Thus, a curvature was made in the specimen by the similar method to that used for bow manufacturing. The change in the curvature was measured when the specimen was forcibly straightened. Blackbutt could not be subjected to the test because it is so weak in terms of bending that experiments under the same conditions as used for the other wood species were impossible.

Table 1-4 shows the curvatures of each wood species immediately after bending in the drying oven. The curvature varied among wood species despite using the same implement.

Figure 1-11 shows the change in the curvature over time when specimens were straightened between two flat steel plates. The line for pernambuco had a gentle slope and was located on the upper part of the graph. Thus, pernambuco tends to maintain its curvature compared with other wood species, although the difference

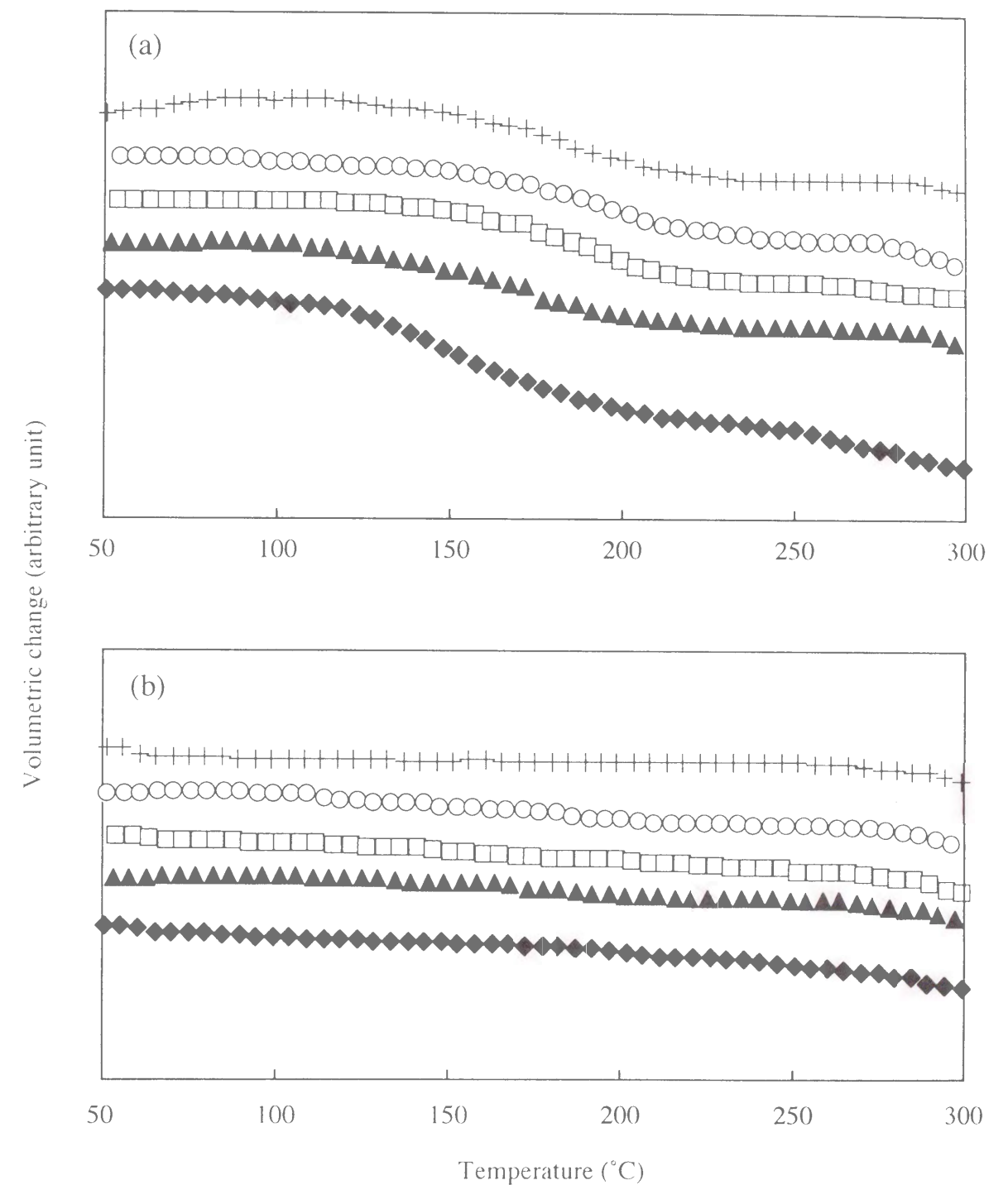


Fig. 1-10. Thermal softening diagrams of wood meals before (a) and after (b) extraction. Legends are the same as Fig. 1-4.

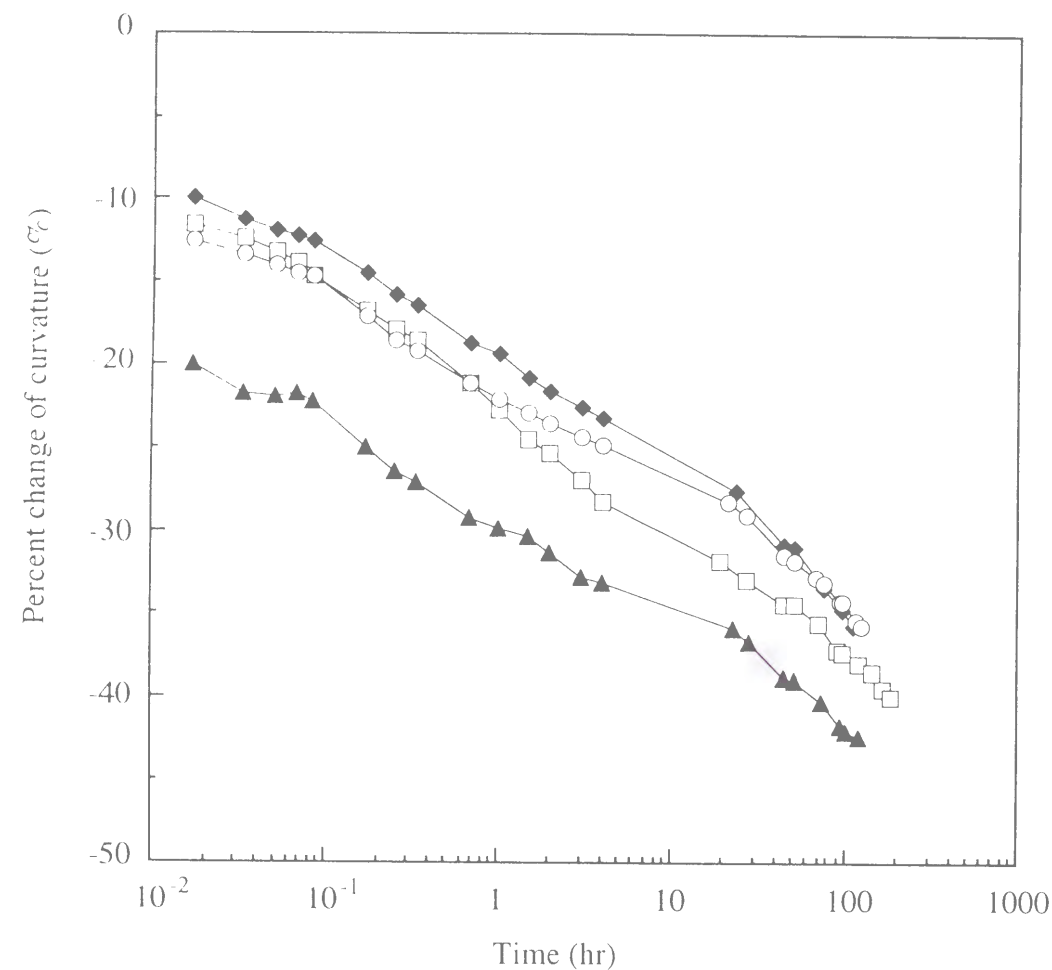


Fig. 1-11. Percent change of the curvature with the passage of time. Legends are the same as in Fig. 1-4.

between pernambuco and other wood species is only slight. Therefore, it is difficult to assert that pernambuco keeps its curved form more than the other wood species. Ultimately, the ease of bending in the flame and permanent retention of the form are not always the primary characteristics for the selection of wood for bow material.

Table 1-4. Curvature immediately after removal of bending device.

	Number	Curvature (m^{-1})	
		m.v.	s.d.
Pernambuco	8	4.12	0.19
Massaranduba	5	4.87	0.09
Kerandji	5	4.66	0.65
Pao rosa	5	6.07	0.25

m.v.; mean value, s.d.; standard deviation.

1.3.7 Shearing strength

One of the most serious problems with bows is a broken head, which is mostly caused by careless handling. For example, if the bow collides perpendicularly with a wall or the floor, the hook-shaped head may be subjected to a shearing impact.

Figure 1-12 shows the relationship between specific gravity in an oven-dried state and the shearing strength of tangential sections of all the wood species. It was found that the shearing strength is proportional to the specific gravity; the shearing strength of pernambuco was somewhat higher than that of the other wood species at the same specific gravity. When the shearing strength is divided by the specific gravity (σ_s/γ), that of pernambuco was highest, although the massaranduba has the highest shearing strength (Table 1-5). In fact, it has been pointed out that bow

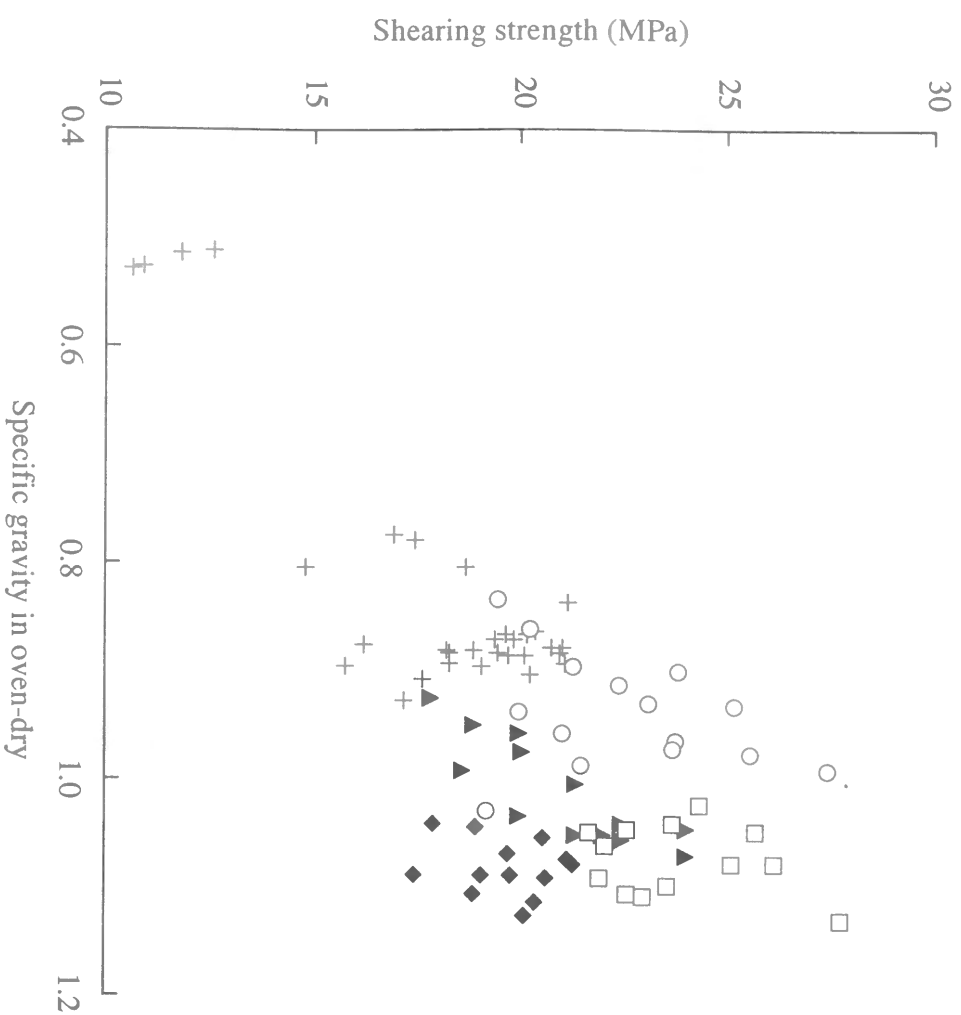


Fig. 1-12. Relationship between specific gravity in oven-dry and shearing strength. Legends are the same as Fig. 1-4.

Table 1-5. Properties of the specimens subjected to the shearing test.

	Number	Specific gravity in oven-dry		Shearing strength (MPa)		σ_s / γ (MPa)
		m.v.	s.d.	m.v.	s.d.	m.v.
Pernambuco	15	0.940	0.052	22.5	2.4	24.0
Massaranduba	13	1.075	0.032	23.9	1.9	22.2
Kerandji	14	1.016	0.047	21.1	1.9	20.8
Pao rosa	13	1.082	0.025	19.7	1.2	18.2
Blackbutt	31	0.825	0.124	18.0	3.0	21.8

m.v.; mean value, s.d.; standard deviation.

heads made of kerandji, whose shearing strength is lower than that of pernambuco, easily break. Pernambuco, with its high shearing strength, seems to satisfy one of the requirements for bow material.

1.3.8 Indentation hardness

Table 1-6 shows the mean values and standard deviations of specific gravity in oven-dry and indentation hardness of the specimens subjected to the measurement of hardness. The indentation hardness of each specimen was averaged between the values in radial and tangential surfaces. The mean values of indentation hardness of kerandji and blackbutt were somewhat lower, and that of pernambuco was higher than others. The hardness is generally proportional to the specific gravity, and the result illustrated in Fig. 1-13 is consistent with this fact. However, the hardness of pernambuco was somewhat higher at the same level of specific gravity than the other wood species. The specific indentation hardness (H/γ), namely indentation hardness divided by specific gravity, was also high for pernambuco (Table 1-6). Hardness is generally also a measure of resistance against the shaving by edged tools. Therefore, pernambuco may be convenient for the delicate adjustment of diameter of the bow. High hardness is naturally favorable from the viewpoint of mechanical strength, that is resistance to be hurt. Nevertheless, the hardness would not be the most preferential factor for the substance of the bow.

Table 1-6. Properties of the specimens subjected to the indentation hardness test.

	Number	Specific gravity in oven-dry		Indentation hardness (MPa)		H/γ (MPa)
		m.v.	s.d.	m.v.	s.d.	
Pernambuco	30	0.935	0.063	63.4	9.1	67.8
Massaranduba	30	1.060	0.021	63.4	5.0	59.8
Kerandji	6	0.909	0.039	45.4	3.3	49.9
Pao rosa	3	0.977	0.003	60.1	2.1	61.5
Blackbutt	18	0.833	0.117	35.7	8.0	42.9

m.v.; mean value, s.d.; standard deviation.

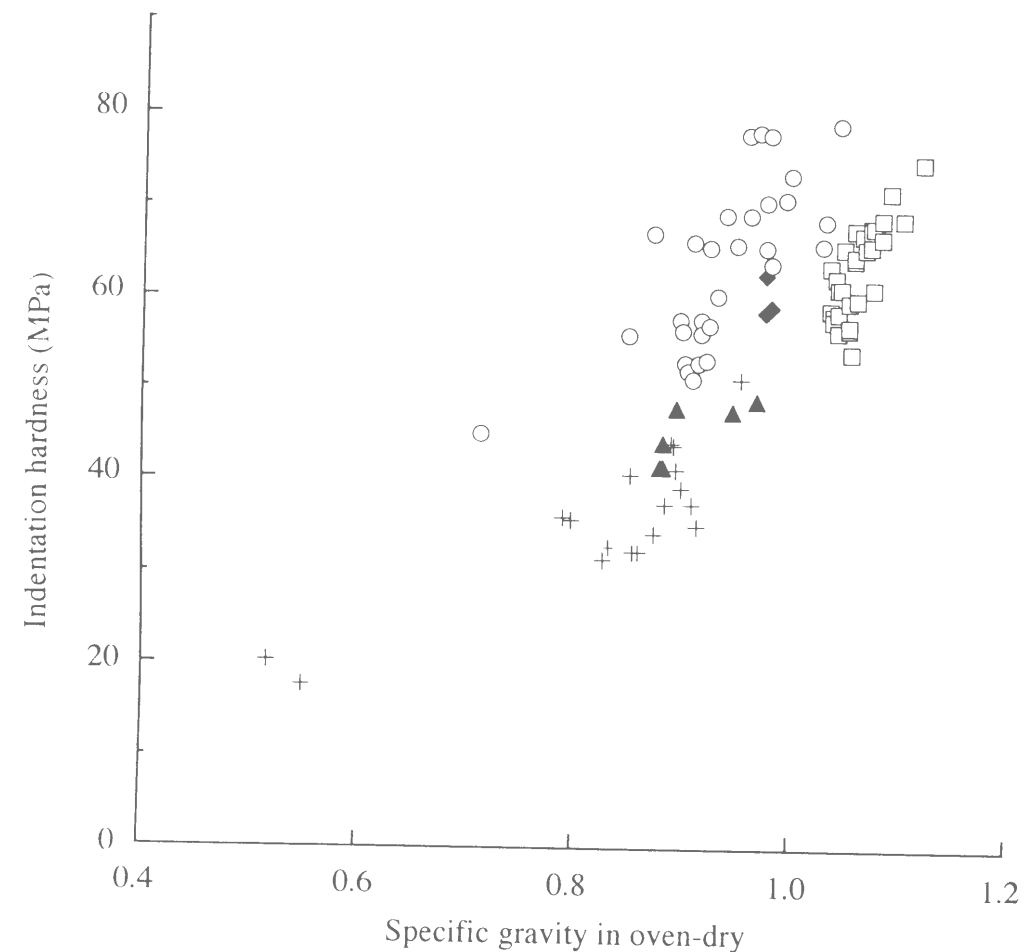


Fig. 1-13. Relationship between specific gravity in oven-dry and indentation hardness. Legends are the same as in Fig. 1-4.

1.4 Summary

Physical and mechanical properties of pernambuco were compared with those of many common hardwoods as well as alternative wood species for bow materials. The $\tan \delta$ of pernambuco was much lower than that of the other wood species, moreover it did not scatter widely among specimens. Therefore, low $\tan \delta$ value seems to be necessary for bow's material, meanwhile Young's modulus is enough if only the bow can sustain the tension of horse hair within the limitation of cross sectional figure. Pernambuco has high content of the water extractives, and the presence of extractives affects the thermal bending of wood material. However, the ease of handling and permanent retention of the curvature when pernambuco is used are not markedly superior. Consequently, these properties are probably not the most important properties when selecting bow material. The shearing strength and indentation hardness of pernambuco was higher than that for the other wood species at the same specific gravity. A high shearing strength and indentation hardness are advantageous for the prevention of damage. These properties seem to be necessary for bow material, but not to be the most important properties.

Chapter 2 Effect of Extractives of Pernambuco on the Vibrational Properties

2.1 Introduction

In the previous chapter, the physical and mechanical properties of pernambuco were compared with those of many other wood species and tried to clarify why pernambuco is suitable for the violin bows. Because the $\tan \delta$ of pernambuco is exceptionally low among wood species examined, it was suggested that a low $\tan \delta$ value is a necessary condition for bow material.

The extremely low $\tan \delta$ of pernambuco may be caused by a large amount of extractives contained. There is a few reports about the effect of extractive components on the physical properties of wooden substances, especially on vibrational properties. Yano (1994) reported that the vibrational properties of Western red cedar (*Thuja plicata*) changed due to an extraction with methanol. Obataya *et al.* (1995a, 1995b) also reported that the $\tan \delta$ of cane (*Arundo donax* L.) used for reeds of woodwind instrument decreased after removal of water-soluble extractives. From these reports, it is obvious that extractive components may exert some effects on the vibrational properties of wood material. However, the extractive components are so different from one wood species to another that the effect also appears to vary greatly depending on the species.

The $\tan \delta$ is also affected by the microfibril angle of the middle layer in the secondary wall. It has been reported that specimens with a large microfibril angle have a larger $\tan \delta$ value (Ono *et al.* 1983, Norimoto *et al.* 1986). Therefore, the microfibril angle of pernambuco may be very low.

In this chapter, the reason why the $\tan \delta$ of pernambuco is peculiarly low is considered from the point of view of the extractive components and microfibril

angle.

2.2 Materials and Methods

2.2.1 Materials

Pernambuco and four substitutable wood species were used for color measurement and X-ray diffractometry. The details of each wood species are described in 1.2.1. Only pernambuco was subjected to the vibrational test and analysis of extractive components.

2.2.2 Vibrational test after extraction with water

Sixty pieces of pernambuco specimens were randomly selected out of the specimens subjected to the vibrational test (1.2.3). Half of them was used for extraction with cold water. The specimens were soaked in water (1 ℓ) and extracted at room temperature for 2 weeks. The water was exchanged twice in a day. The other half was extracted with boiling water (1 ℓ) for 48 hours exchanging the water with fresh boiling water for every 3 hours. After drying under ambient conditions and subsequent drying at 60 °C under vacuum for two days, weight loss of the specimens was measured. Then the specimens were conditioned at 20 °C and 65% R.H. for two weeks, and the vibrational properties were tested again by the methods described in 1.2.3.

2.2.3 Color measurement

Color measurements were carried out on the specimens after the vibrational or hardness test described in 1.2.3 and 1.2.8, respectively. A color meter (Nippon Denshoku Kogyo Co., LTD. Z-1001 type DP) was used. The CIE $L^*a^*b^*$ scales were adopted to describe the mean visual judgments of color appearance. Color

values were taken as the average of three measuring spots (10 mm in diameter) on each specimen.

2.2.4 X-ray diffractometry

The mean microfibril angle (MMA) was evaluated by X-ray diffractometry. Specimens of 1 mm (L) × 0.8 mm (R) × 2 mm (T) were used. It is known that Cave's method (Cave 1966) and improved Cave's method (Yamamoto 1993) are convenient for determining the MMA of a cell wall.

A point-focused X-ray beam (Cu-K α X-ray, power 30 mA × 40 kV) was applied to the tangential surface of each specimen. An X-ray diffraction apparatus (RINT2200V; Rigaku Denki) was used. An imaging plate (Fuji Film Blue IP) was set behind the specimen to record the X-ray diffraction pattern. The MMA was calculated from a diffraction intensity distribution around (200) arc using the Cave's method. Five specimens were measured for respective wood species.

2.2.5 Analysis of water-soluble extractives of pernambuco

General methods

Thin layer chromatography (TLC) and preparative thin layer chromatography (PTLC) were performed on silica gel plates (Kieselgel 60 F₂₅₄, Merck), and the spots were detected under UV light (254 nm). ¹H-NMR spectra was recorded with a Bruker AC300 FT-NMR (300 MHz) spectrometer, in chloroform-*d* or deuterium oxide with tetramethylsilane (TMS) as an internal standard. Chemical shifts (δ) and coupling constants (*J*) are given in δ values (ppm) and Hz, respectively. The following abbreviations are used: s = singlet, d = doublet, dd = double doublet. Optical rotations were measured at 28 °C using a JASCO Dip-1000 digital polarimeter. Electron impact-mass spectroscopy (EI-MS) was performed on a

Shimadzu GC-MS QP-1000.

Structural analysis of extractive components

The wood meal of pernambuco (2.96 g) was extracted by soaking in water (20 ml) with stirring at ambient temperature for 24 hours. The supernatant was separated by filtration, and freeze-dried to give extractives (76.9 mg) as a red-brown powder. The extractives were checked by TLC developed with MeOH/CHCl₃ (1/4, v/v). Two major spots were detected (*R_f* values: 0.51 (compound **1**); 0.33 (compound **2**)) under UV light. Then the crude extractives were purified by a silica gel column (Wakogel C-200, 200 mm in length and 25 mm in inside diameter) eluted with ethyl acetate/*n*-hexane/methanol (11/8/1, v/v/v) to afford fractions **1** (7.8 mg) and **2** (44.0 mg). The fraction **1** contained compound **1** as almost pure, checked by TLC. The fraction **2** consisted of compound **2** as a main compound and other impurities. These fractions were acetylated with acetic anhydride (0.5 ml) and pyridine (0.5 ml) at room temperature for overnight, and acetylated fractions **3** (=compound **3**, 12.4 mg) and **4** (61.6 mg) were obtained from the fractions **1** and **2**, respectively. The fraction **4** was chromatographed on TLC developed with MeOH/CHCl₃ (1/19, v/v), and two spots were observed (*R_f* values: 0.49 (compound **4**); 0.35 (compound **5**)). These compounds were purified by PTLC developed with MeOH/CHCl₃ (1/19, v/v) to afford compounds **4** (4.5 mg) and **5** (25.9 mg) as a pure.

Measurement of the proportion of main compounds

The other new extractives were separated into two fractions, compounds **1**- and **2**-predominant fractions, by a silica gel column (Wakogel C-200) developed with ethyl acetate/*n*-hexane/methanol (11/8/1, v/v/v), then each fraction was analyzed by a high performance liquid chromatograph (HPLC). A Shimadzu liquid

chromatograph injector (LC-10ATvp), a Shimadzu column oven (CTO-10Avp), a Shimadzu UV-VIS detector (SPD-10Avp), a Shimadzu refractive index detector (RID-10A), a Shimadzu communication bus module (CBM-10A), a Shimadzu LC workstation (CLASS-LC10), and a column (nacalai tesque COSMOSIL 5C₁₈-MS) were used. The elution condition was as follows: eluent, MeOH/0.02M phosphate buffer solution (pH 7.0) (95/5, v/v); flow rate, 1.0 ml/min; column temperature, 40 °C.

Compound 1. EI-MS m/z (%): 318 (M⁺, 30.4), 286 (100), 268 (47.5), 229 (28.2). ¹H-NMR (300 MHz, D₂O): δ 2.87 (1H, d, J = 16.08; C₇-H) and 3.07 (1H, d, J = 16.14; C₇-H), 3.68 (1H, d, J = 11.72; C₆-H) and 4.00 (1H, d, J = 11.86; C₆-H), 4.05 (1H, s; C₁₂-H), 6.41 (1H, d, J = 2.02; C₄-H), 6.65 (1H, dd, J = 2.08, 8.37; C₂-H), 6.78 (1H, s; C₁₁-H), 6.82 (1H, s; C₈-H), 7.35 (1H, d, J = 8.28; C₁-H).

Compound 2 (Fraction 2). $[\alpha]^{28}_{\text{D}}$ -10.6° (c = 2.14, in methanol). EI-MS m/z : 304 (M⁺, 100), 243 (25.8), 229 (48.2). The ¹H-NMR spectrum was complicated because of impurities.

Compound 3 (Acetylated compound 1). ¹H-NMR (300 MHz, CDCl₃): δ 2.08 (3H, s; OAc), 2.26 (6H, s; OAc × 2), 2.29 (3H, s; OAc), 3.45 (2H, s; C₇-H₂), 3.73 (1H, d, J = 12.29; C₆-H) and 4.76 (1H, dd, J = 1.84, 12.31; C₆-H), 4.47 (1H, s; C₁₂-H), 6.66 (1H, d, J = 2.31; C₄-H), 6.80 (1H, dd, J = 2.32, 8.32; C₂-H), 7.05 (1H, s; C₁₁-H), 7.09 (1H, s; C₈-H), 7.36 (1H, d, J = 8.62; C₁-H).

Compound 4 (Acetylated compound 2). $[\alpha]^{28}_{\text{D}}$ -59.3° (c = 1.59, in chloroform). EI-MS m/z : 514 (M⁺, 56.0), 472 (100), 430 (91.5), 388 (38.1), 310

(35.0), 268 (37.2), 229 (32.1). ¹H-NMR (300 MHz, CDCl₃): δ 2.03 (3H, s; OAc), 2.10 (3H, s; OAc), 2.30 (9H, s; OAc × 3), 2.71 (1H, d, J = 14.11) and 3.49 (1H, d, J = 14.09), 3.99 (1H, d, J = 12.78) and 4.51 (1H, d, J = 12.76), 4.43 (1H, d, J = 11.97) and 4.84 (1H, d, J = 11.96), 6.85 (1H, d, J = 2.11), 6.88 (1H, dd, J = 2.31, 8.41), 7.09 (1H, s), 7.19 (1H, s), 7.24 (1H, d, J = 8.46).

Compound 5 (Acetylated compound 2). $[\alpha]^{28}_{\text{D}}$ -38.7° (c = 2.57, in chloroform). ¹H-NMR (300 MHz, CDCl₃): δ = 2.12 (3H, s; OAc), 2.31 (9H s; OAc × 3), 2.74 (2H, s), 3.91 (1H, d, J = 12.29) and 4.33 (1H, d, J = 12.28), 4.14 (2H, s), 6.88 (1H, d, J = 2.24), 6.92 (1H, dd, J = 2.30, 8.35), 7.16 (1H, s), 7.18 (1H, s), 7.28 (1H, d, J = 8.44).

2.3 Results and Discussions

2.3.1 Change of vibrational properties after extraction with water

The mean values of weight loss were 5.1% and 16.1% for cold water extraction and hot water extraction, respectively.

Figure 2-1 shows the relationship between weight loss and percent change in vibrational properties as a result of extractions. The E'/γ decreased about 1 to 10% regardless of weight loss (Fig. 2-1(a)). On the other hand, the percent change in $\tan \delta$ increased with increasing the weight loss up to about 150% (Fig. 2-1(b)). It is apparent that the extractives greatly lowered $\tan \delta$ of pernambuco. According to Akitsu *et al.* (1991), $\tan \delta$ decreased when the hydrophobic or rigid molecules were introduced into cell walls, while it increased when the bulky and flexible molecules were introduced. They also reported that the $\tan \delta$ increased when the chemicals only filled up cell lumens. Therefore, it is probable that the chemical

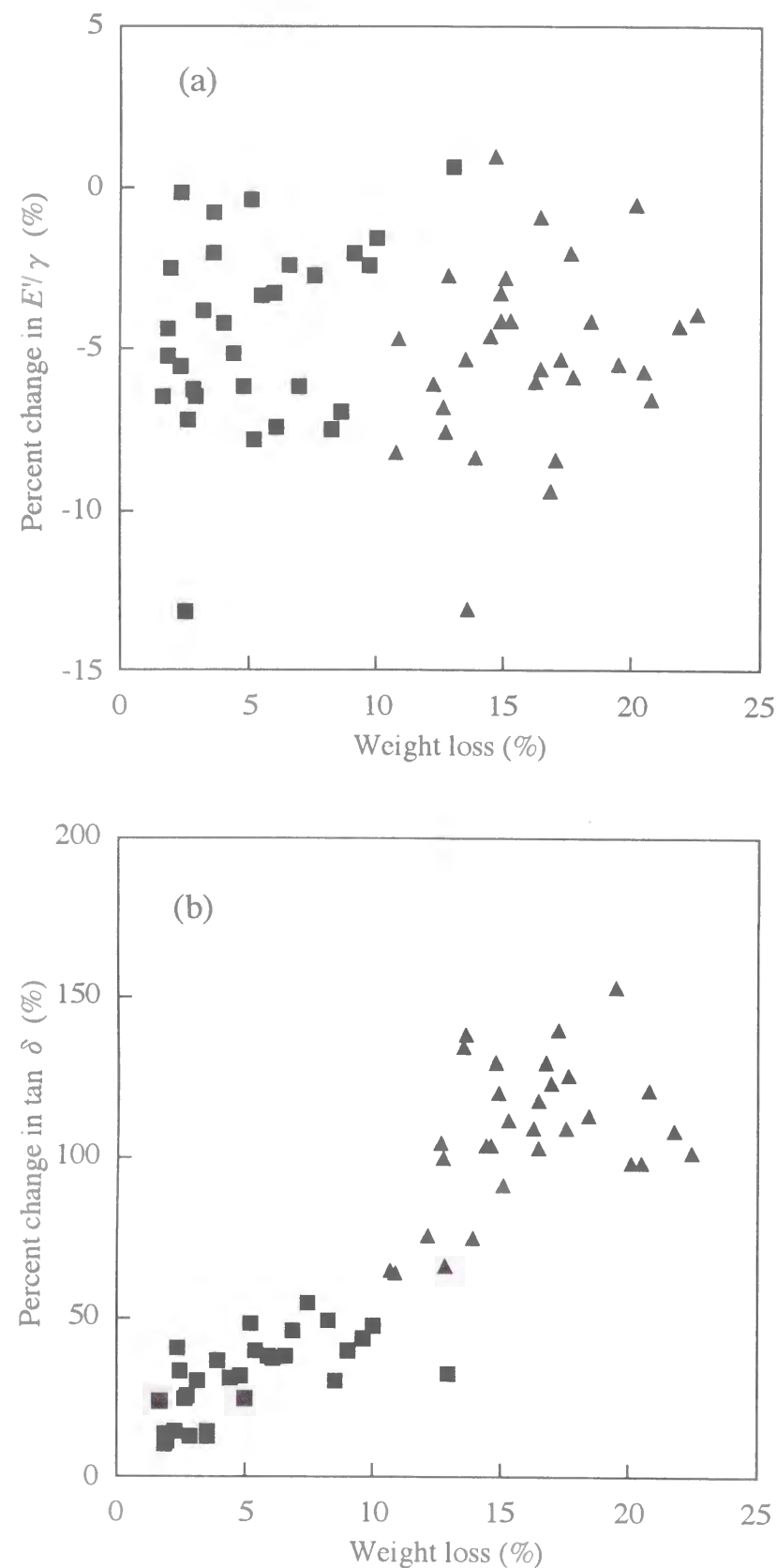


Fig. 2-1. Relationship between weight loss and percent change in E'/γ (a) or $\tan \delta$ (b). \blacktriangle ; Hot water extraction, \blacksquare ; Cold water extraction.

structure and/or deposited location of extractives of pernambuco satisfy the necessities for lowering the $\tan \delta$.

The relationship between E'/γ and $\tan \delta$ before and after water extraction is shown in Fig. 2-2. The plots sifted the position to upper direction after each extraction. Especially, $\tan \delta$ increased greatly by the hot water extraction which brought about large weight loss. Eventually, it is concluded that the extractives is a cause of low $\tan \delta$ value of pernambuco.

2.3.2 Relationship between wood color and properties

Figure 2-3 shows the relationship between redness (a^*) and yellowness (b^*) for all wood species. The plots for pernambuco were scattered widely. This figure describes that the color tone of pernambuco differed greatly among individual test specimens. For the pernambuco, the correlation coefficient between a^* and $\tan \delta$ ($r=-0.339$) was significant (Fig. 2-4). Relationship between wood color and extractives content was reported for blackbutt by Yazaki *et al.* (1994). The a^* is probably dependent upon the extractives content also for pernambuco. Therefore, the fact that a^* is inversely proportional to the $\tan \delta$ suggests the indirect correlation between extractives content and $\tan \delta$. The lightness (L^*) and yellowness (b^*) had no significant correlation with other properties.

2.3.3 Mean microfibril angle

The middle layer in the secondary wall (S_2 layer) comprises 80% or more of the volume of the cell wall of wood fiber, and some of the physical properties of wood depend strongly on the microfibril angle of S_2 layer. Though the high extractives content of pernambuco is responsible for a low $\tan \delta$ value, the microfibril angle must also be taken into consideration.

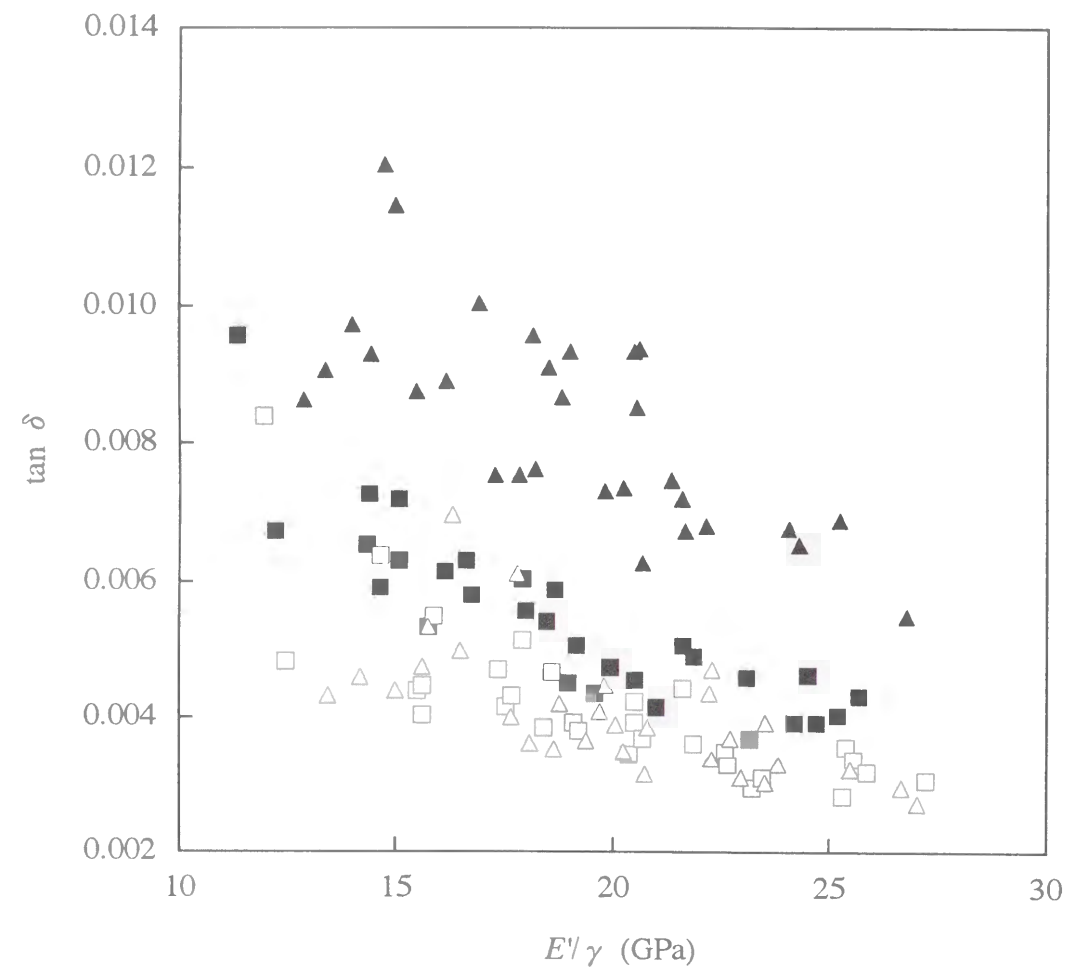


Fig. 2-2. Effect of the water extractions on the relationship between E'/γ and $\tan \delta$. \triangle ; Before hot water extraction, \blacktriangle ; After hot water extraction, \square ; Before cold water extraction, \blacksquare ; After cold water extraction.

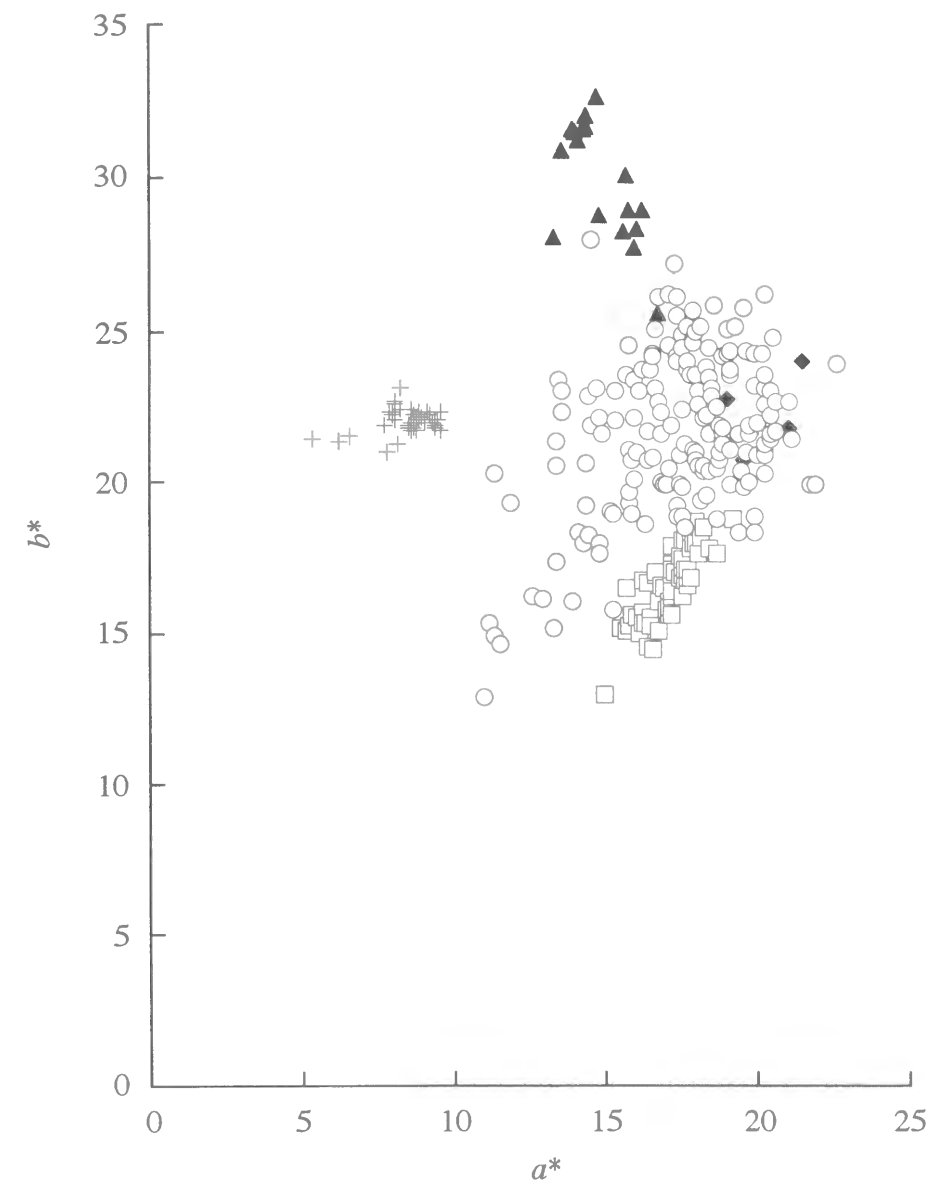


Fig. 2-3. Relationship between redness (a^*) and yellowness (b^*). \circ ; Pernambuco, \square ; Massaranduba, \blacktriangle ; Kerandji, \blacklozenge ; Pao rosa, $+$; Blackbutt.

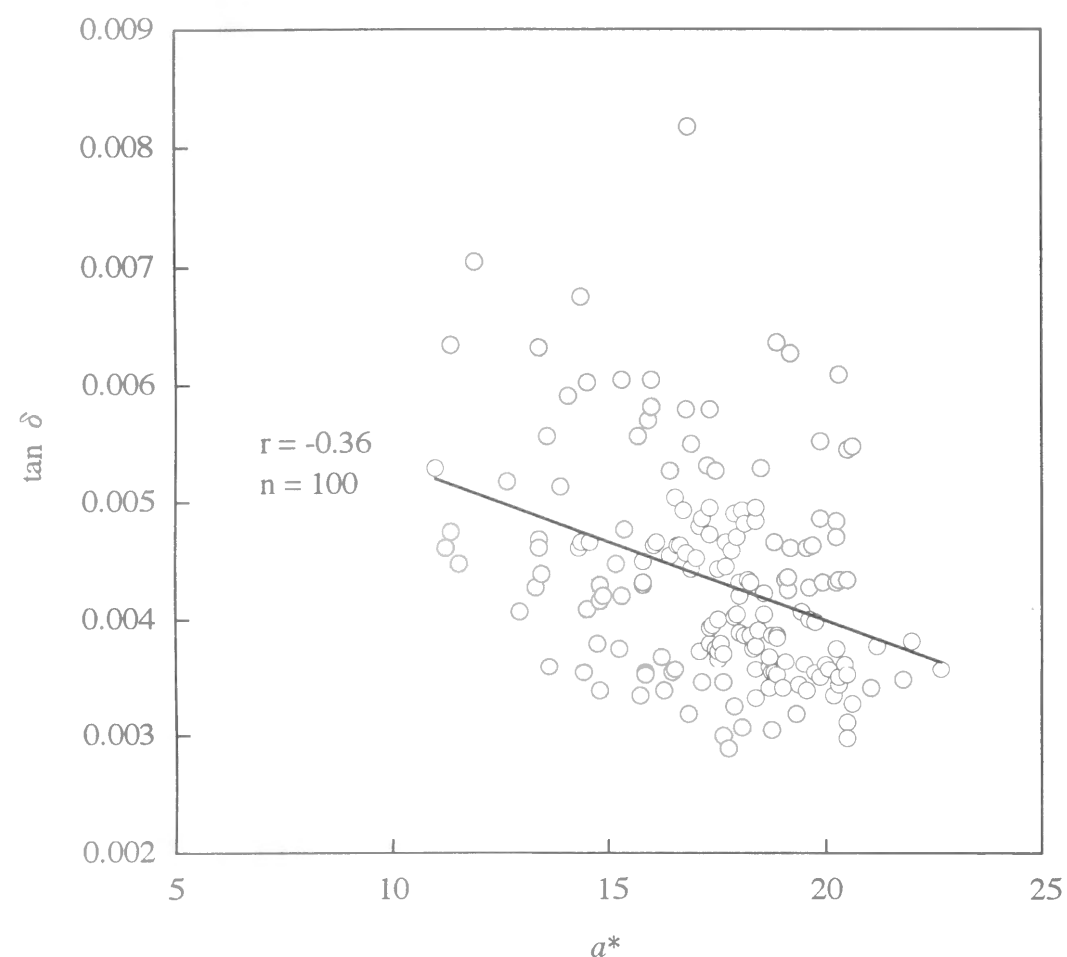


Fig. 2-4. Relationship between redness (a^*) and $\tan \delta$ of pernambuco. r ; correlation coefficient, n ; number.

The MMA estimated by Cave's method is shown in Table 2-1. The $\tan \delta$ values and extractives contents are from Tables 1-2 and 1-3, where other parts of the same specimens were used. Though the wood species examined here have a high specific gravity, it is probable that the calculated values for the microfibril angle are lower than the true values because the thick cell wall may increase the diffraction intensity. The MMA in Table 2-1 is available only when high specific-gravity species are compared.

The MMA value for pernambuco and massaranduba were nearly equal, although the $\tan \delta$ for pernambuco was less than half of that for massaranduba. From the viewpoint of the MMA, $\tan \delta$ for pernambuco and massaranduba ought to be equal; therefore it is thought that the large amount of extractives in pernambuco lowers its $\tan \delta$. On the other hand, among the five wood species examined the $\tan \delta$ for pao rosa was not particularly large, although its MMA was high. This point is explainable if a large amount of extractives involved in pao rosa lowers the $\tan \delta$.

2.3.4 Analysis of water-soluble extractives of pernambuco

The $^1\text{H-NMR}$ spectrum of the compound **3** coincided with that of the brazilin tetraacetate (Craig *et al.* 1965) thoroughly. Moreover, molecular weight (286) of compound **1** coincided with that of brazilin ($\text{C}_{16}\text{H}_{14}\text{O}_5$, Fig. 2-5). From these results, **1** was identified with brazilin which has been reported to be contained in Brazil-wood, species *Caesalpinia* (Gilbody *et al.* 1901, Perkin *et al.* 1928).

The $^1\text{H-NMR}$ spectrum and molecular weight (514) of the compound **4** coincided with that of the protosappanin B pentaacetate (Nagai *et al.* 1986). The optical rotation ($[\alpha]^{28} -59.3^\circ$ (CHCl_3)) of **4** was almost the same as that of protosappanin B pentaacetate reported by Nagai *et al.* ($[\alpha]_D^{25} -62.5^\circ$ (CHCl_3)).

Table 2-1. Mean Microfibril angle, $\tan \delta$ and extractives content.

	Number of specimen	MMA (°)	$\tan \delta$	Extractives content (%)	
				Hot water	Ethanol-benzene
Pernambuco	5	12.53	4.12×10^{-3}	13.0	9.2
Massaranduba	5	12.58	10.04	6.5	4.2
Kerandji	5	9.50	5.74	7.3	5.4
Pao rosa	5	21.24	7.41	10.2	21.2
Blackbutt	5	8.91	6.20	6.0	1.7

MMA; Mean microfibril angle.

The values for $\tan \delta$ and content of extractives are from Tables 1-2 and 1-3, respectively.

Compound **5** has four acetyl groups, and showed same $^1\text{H-NMR}$ spectrum of compound **4** after acetylation at 60°C for overnight. The optical rotation of **5** ($[\alpha]^{28} -38.7^\circ$ (CHCl_3)) was almost equal to that of protosappanin B tetraacetate reported by Nagai *et al.* ($[\alpha]_D^{25} -36.8^\circ$ (CHCl_3)). Therefore, **5** was found to be protosappanin B tetraacetate. From these results, **2** was identified with protosappanin B ($\text{C}_{16}\text{H}_{16}\text{O}_6$, Fig. 2-5) which has been found in the heartwood of sappan (*Caesalpinia sappan* L.) by Nagai *et al.* (1986). Though compound **2** contained a small quantity of impurities, the optical rotation ($[\alpha]^{28} -10.6^\circ$ (MeOH)) and molecular weight (304) of compound **2** coincided with those of protosappanin B reported by Nagai *et al.* ($[\alpha]_D^{15} -11.4^\circ$ (MeOH)).

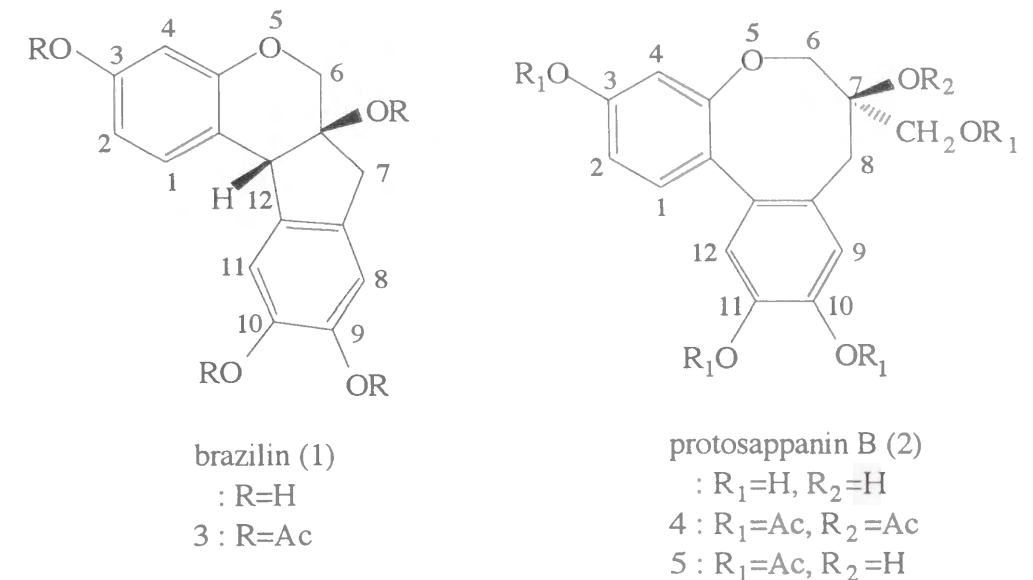


Fig. 2-5. Main extractives of pernambuco, and these acetylated compounds.

Protosappanin B and brazilin were quantitatively analyzed by the HPLC. It was roughly estimated that the amount of protosappanin B and brazilin were 40% and 10% of the whole extractives, respectively. However, exact contents of main components were not determined because the peaks of impurities could not be separated thoroughly from that of main component.

2.4 Summary

This chapter was focused on the peculiarity of the $\tan \delta$ of pernambuco. The correlation between vibrational properties and extractive components was preponderantly examined. The $\tan \delta$ of pernambuco increased after extraction with water. The percent change in $\tan \delta$ was proportional to the weight loss. This suggested that, the low $\tan \delta$ of pernambuco is related closely with the contained water-soluble extractives. The low $\tan \delta$ value of pernambuco seems to be attributable to the high extractives content rather than to the small microfibril angle. Chemical structures of the water-soluble extractives of pernambuco were analyzed, and two main components, protosappanin B and brazilin, were found. In particular, protosappanin B occupied about 40% of extractives of pernambuco.

Chapter 3 Vibrational Property Changes of Spruce Wood by Impregnation with Extractives of Pernambuco

3.1 Introduction

In Chapter 2, it was described that low $\tan \delta$ of pernambuco is attributable to the extractive components contained in great quantities. Although the $\tan \delta$ of wood may also vary with the mean microfibril angle, the influence of extractive components was the main factor as far as pernambuco is concerned. However, the possibility cannot be ruled out that the change of fine structure of wood after removing of extractive components may also influence the $\tan \delta$. If the extractive components of pernambuco have the main lowering effect on $\tan \delta$, one should be able to decrease the $\tan \delta$ of any other wood species simply by impregnation with the extractives of pernambuco.

In this chapter, the effects of the pernambuco extractives impregnated into the other wood species is discussed on the vibrational properties. Further, the mechanism which controls the vibrational properties of wood impregnated with extractives is discussed.

3.2 Materials and Methods

3.2.1 Materials

Sitka spruce (*Picea sitchensis* Carr.) specimens were made into a size of 150 mm (L) \times 12 mm (R) \times 2 mm (T). There were 88 specimens. Before treatments with the extractive components, vibrational properties were measured by the method described in 1.2.3.

3.2.2 Preparation of water-soluble extractives from pernambuco

Heartwood of pernambuco was ground by a Wiley mill, and only the fraction that passed through a sieve with 355 μ m apertures but was retained by a sieve with 150 μ m apertures was used. The wood meal was extracted by soaking in water with occasional stirring at ambient temperature for 24 hours. The supernatant water was collected by decanting. Then fresh water was added for further extraction. The extraction was repeated 10 times. The combined supernatant was concentrated using a rotary vacuum evaporator at about 40 °C to prevent chemical changes of the extractives. After removing the precipitates by centrifugation, extractives in the supernatant were obtained as a red-brown powder by freeze-drying the highly concentrated solution. From about 480 g (oven-dried) of wood meal, approximately 65 g of extractive was obtained (yield: 13.5 %).

3.2.3 Treatments of spruce wood with water-soluble extractives of pernambuco

Specimens of Sitka spruce were treated with an aqueous solution of extractives obtained from pernambuco by the following two ways.

Impregnation under evacuation

Three or four specimens were soaked in aqueous solutions of the extractives with concentrations of 20.9, 25.7, 33.8, 51.4 and 102.8 g/ ℓ for eight days with occasional evacuation using an aspirator. After drying under ambient conditions and subsequent drying at 60 °C under vacuum for two days, the weight percent gain (WPG) and percent increase of oven-dried volume (bulking) of the specimens were measured. The specimens were then conditioned at 20 °C and 65% R.H. for two weeks and the vibrational properties were measured again. There were 36 specimens subjected to this treatment.

Surface application of the aqueous solution of extractives

Aqueous solution of extractives (131.5 g/ ℓ) was uniformly applied by a brush to all surfaces of specimens and then air-dried. This procedure was repeated 2, 5, 7 and 10 times to obtain specimens with different WPG. The WPG, bulking and vibrational properties were measured by the same methods stated for the impregnation treatment. There were 16 specimens subjected to this treatment.

3.2.4 Treatments of spruce wood with isolated extractives of pernambuco

From the wood meal of pernambuco (150 g), approximately 20 g of extractive was obtained by the same method described above (3.2.2). Then the extractives were purified by a silica gel column (Wakogel C-200) developed with ethyl acetate/*n*-hexane/methanol (11/8/1, v/v/v) to afford protosappanin B-predominant fraction (12 g).

Four pieces of Sitka spruce specimens were soaked in each H₂O/MeOH (9/1, v/v) solutions of protosappanin B-predominant fraction whose concentrations are 5, 10, 20 and 40 g/ ℓ for eight days with occasional evacuation using an aspirator. After treatment, WPG and the vibrational properties of the specimens were measured. There were 16 specimens subjected to this treatment.

3.2.5 Treatments of spruce wood with hematoxylin

Commercially available hematoxylin (Fig. 3-1) which is used for a stain for microscopic observation was impregnated. Five kinds of solutions of hematoxylin in concentrations, 5, 10, 20, 30 and 50 g/ ℓ were prepared, and four pieces of specimens were soaked in each solutions for eight days with occasional evacuation using an aspirator. After treatment, WPG and the vibrational properties of the specimens were measured. Twenty pieces of the specimen were used for the treatment.

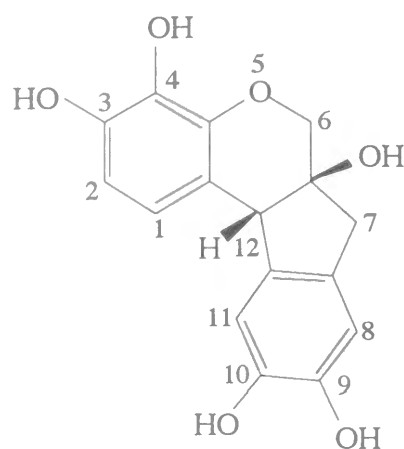


Fig. 3-1. Chemical structure of hematoxylin.

3.2.6 Microscopic observation of filled specimens

A fifty μ m thick cross section was cut from the treated specimen by means of a microtome (Olympus TU-213N). Epoxy resin, which scarcely dissolved the water-soluble extractives of pernambuco, was dropped on the sliced section on a slide glass, and the whole section was covered with glass. The epoxy resin was hardened overnight at 60 °C. The observation was carried out under a microscope (Olympus BH2) at 40 magnifications. For observations at 200 magnifications, thinner section (3 μ m thickness) were prepared.

3.3 Results and Discussion

3.3.1 Topological aspects of the extractives-treated specimens

Relationship between the WPG and bulking of specimens is shown in Fig. 3-2. For the specimens impregnated under evacuation, the bulking increased linearly up to around 15% WPG and then leveled off. This suggests that extractive components are impregnated in the amorphous regions of the cell wall until about 15% WPG, and in cell lumens thereafter. Figure 3-3 shows the cross-sectional views of the

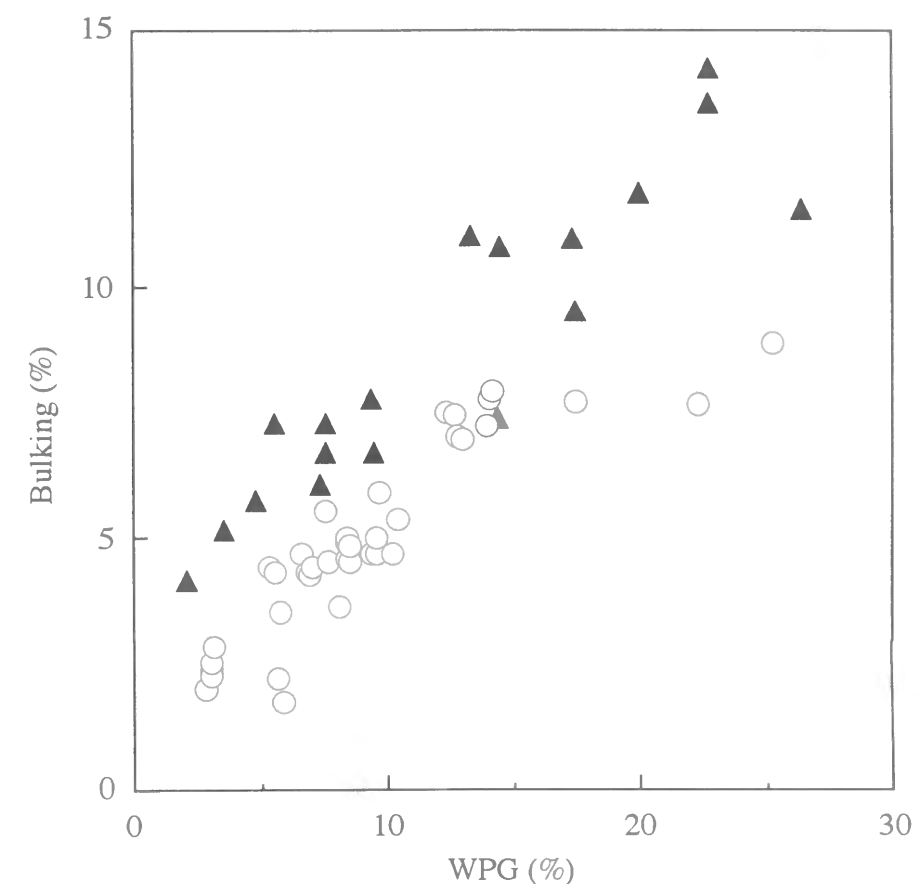


Fig. 3-2. Relationship between weight percent gain (WPG) and percent increase in oven dry volume (bulking).
○; Impregnation, ▲; Surface application.

specimens impregnated to 7.6 and 25.2% WPG. For the specimen whose WPG is 7.6%, extractives did not distribute uniformly in the whole specimen but were limited to within about 0.2 mm of the surface (Fig. 3-3(a)). The late wood was easier to impregnate than the early wood. From the observation of the thinner section at high magnification, it was found that the extractives scarcely deposit in the lumens. On the other hand, for the specimen whose WPG is 25.2%, extractives were impregnated more deeply (Fig. 3-3(b)). Moreover, extractives were observed to deposit even in some lumens in the thinner section at high magnification. These results may explain the change in leveling off of bulking at higher WPG, as observed in Fig. 3-2.

Figure 3-4 shows cross-sectional views of surface-applied specimen with a WPG of 17.3%. The extractives hardly penetrated the specimen. From the observation at high magnification, the extractives surely existed in both cell walls and some lumens at the vicinity of the surface. In Fig. 3-2, the bulking of the surface-applied specimens was somewhat higher than that of impregnated specimens at the same WPG. This seems to arise from the accumulation of applied extractives on the surface but not real bulking of specimens.

3.3.2 Changes of vibrational properties

Figure 3-5 shows the relationship between WPG and percent change in E'/γ as a result of treatments. The E'/γ decreases linearly with increasing WPG in both treated specimens, but the impregnated specimen had a gentle slope. The difference between the two treated specimens is more significant if the percent change in E' is plot as a function of WPG (Fig. 3-6). For the treatment with surface application, E' decreased with the increase in WPG. For impregnated treatment, E' decreased about 5% regardless of the WPG, indicating that the continuous decrease of E'/γ with increasing WPG in Fig. 3-5 is due to the increase in γ . The percent change in

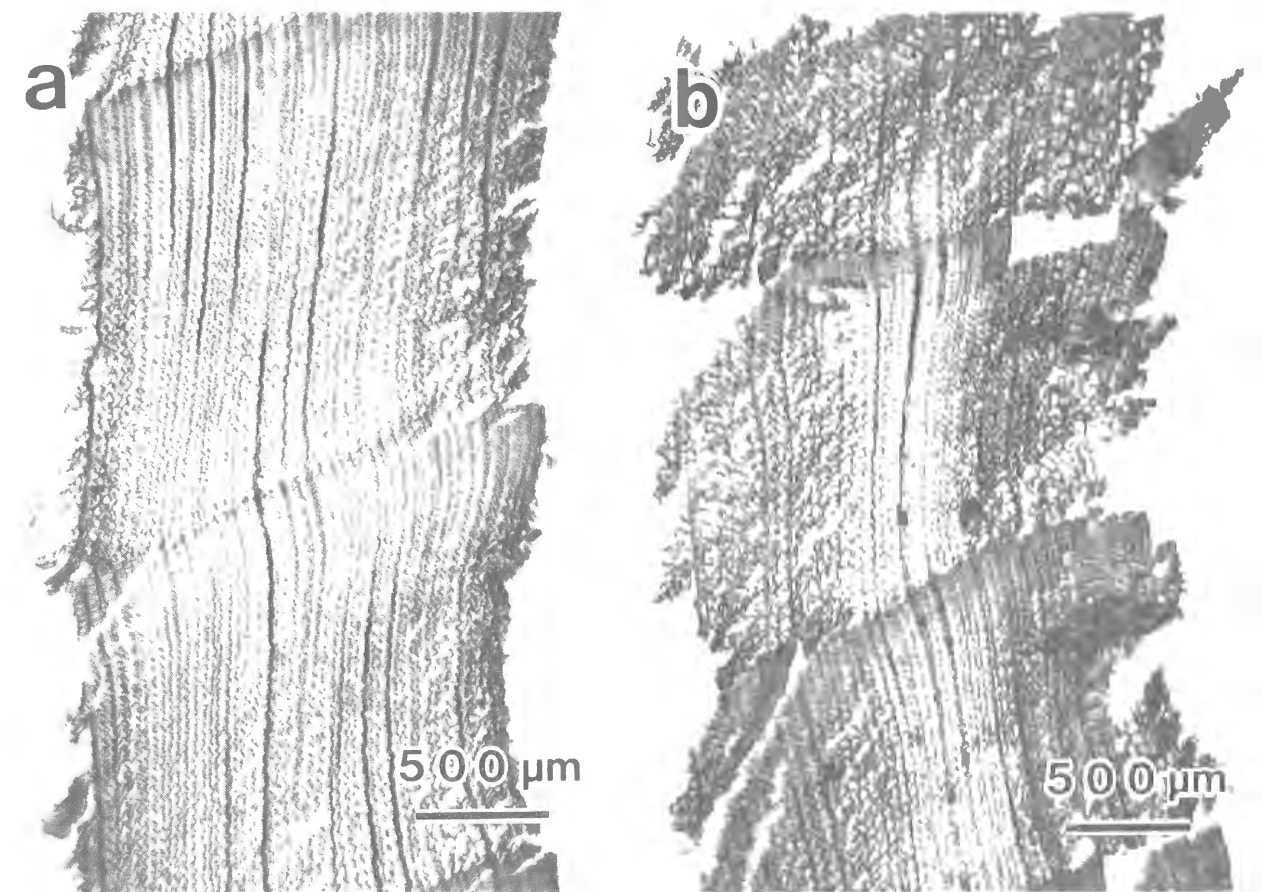


Fig. 3-3. Cross section of the impregnated specimen under evacuation. a; weight percent gain (WPG) is 7.6%, b; WPG is 25.2%.

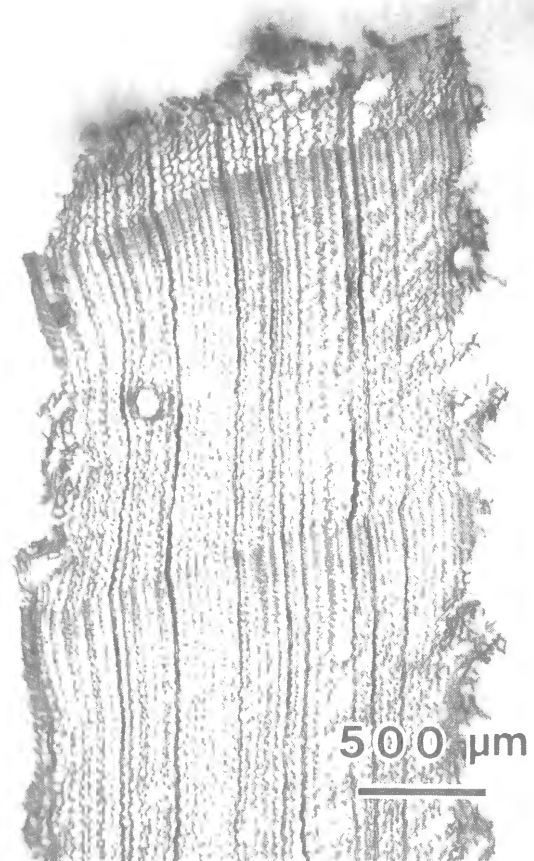


Fig. 3-4. Cross section of the surface-applied specimen (weight percent gain is 17.3%).

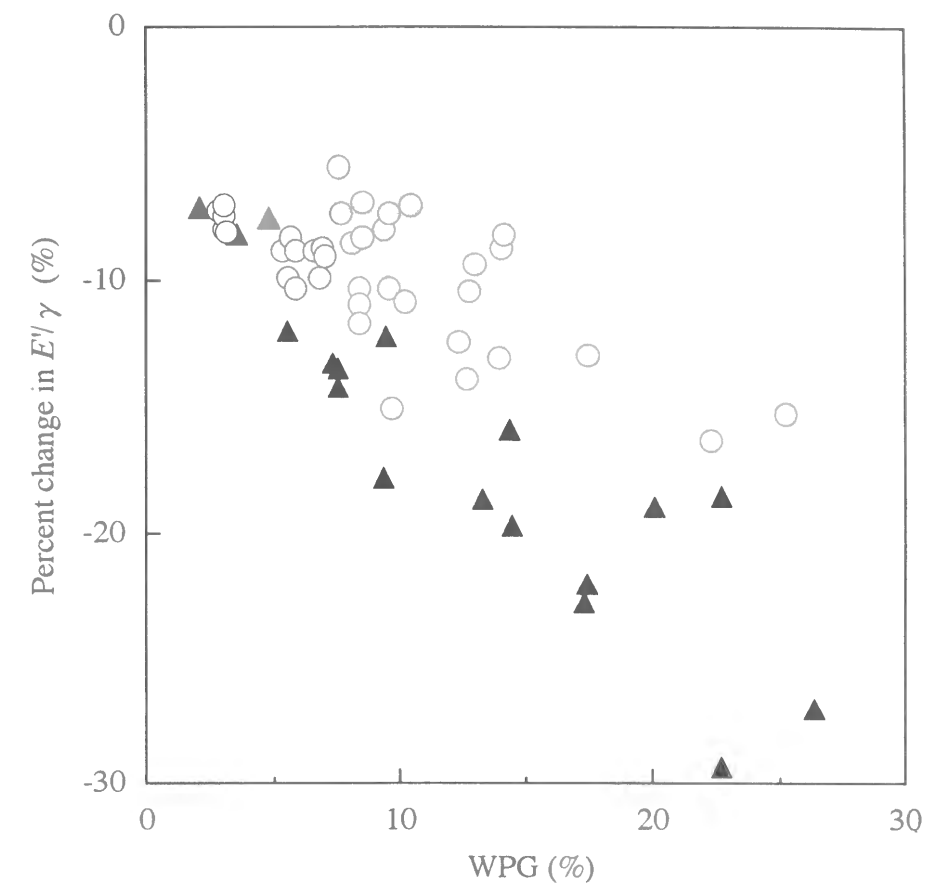


Fig. 3-5. Relationship between weight percent gain (WPG) and percent change in E'/γ . Legends are the same as Fig. 3-2.

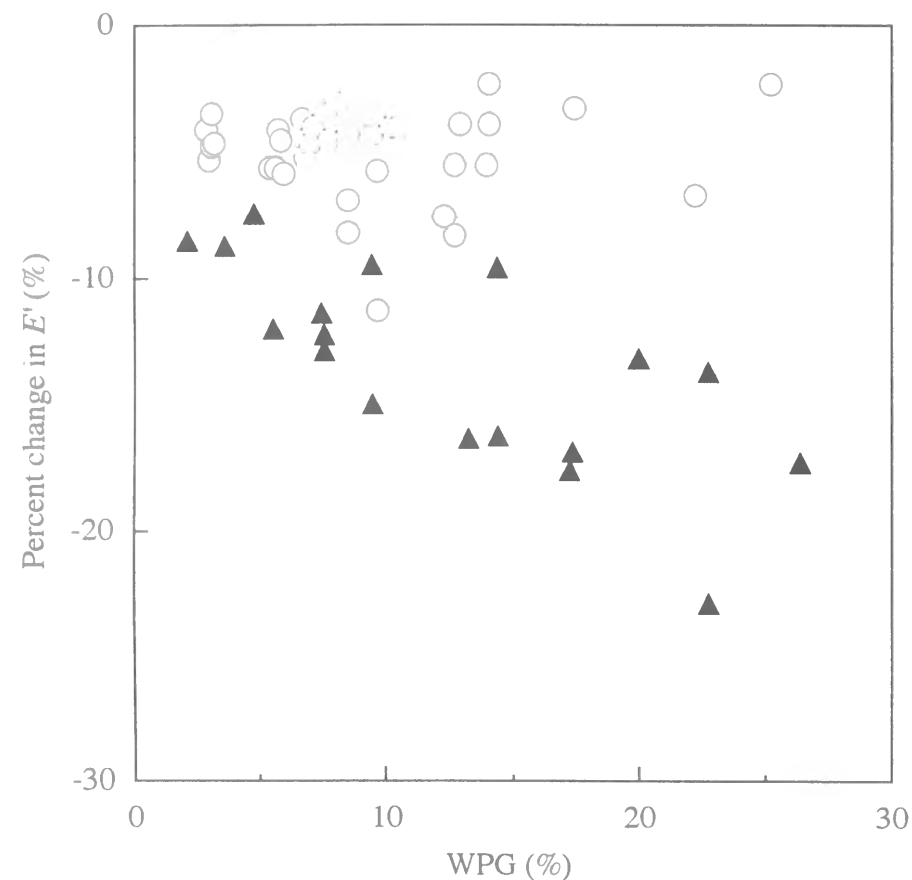


Fig. 3-6. Relationship between weight percent gain (WPG) and percent change in E' . Legends are the same as in Fig. 3-2.

γ for impregnated specimen was from 2.0 % to 14.9 %.

Figure 3-7 shows the relationship between WPG and the percent change in $\tan \delta$. In the case of surface application, $\tan \delta$ of all specimens decreased only 1-10 %, and there was no correlation between WPG and the percent change in $\tan \delta$. On the other hand, the $\tan \delta$ of impregnated specimens decreased significantly (20-47 %), and the $\tan \delta$ decreased with the increase in WPG.

There were some reports that the decrease in $\tan \delta$ was due to chemical treatment. For example, formaldehyde treatment decreased the $\tan \delta$ because of the formation of cross-linkages between neighboring hydroxyl groups of wood components (Yano *et al.* 1986). Treatment with low-molecular-weight phenol formaldehyde resin or maleic acid-glycerol also reduced the $\tan \delta$ (Akitsu *et al.* 1991, 1993), again likely due to cross-linking formation. In this study, because the impregnation was done at room temperature and the successive drying at 60 °C under vacuum, the formation of covalent bonds between impregnated extractives and wood components is improbable under such mild conditions. Therefore, it is plausible that the extractive components impregnated the amorphous region, forming non-covalent but secondary bonds, resulting in the decreased $\tan \delta$. The structural characteristics or molecular weight (or both) of extractive components may also be necessary conditions.

Such secondary bonds must increase the Young's modulus at least in amorphous region of wood; nevertheless the Young's modulus decreased as a whole. This probably arises from the relative decrease of volume fraction of the crystal region, whose Young's modulus is much greater than that of the amorphous region as a result of the expansion of the latter region due to the bulking of impregnated components.

Because the bending property of the specimen influenced its flexural vibration, it is supposed that the surface characteristics dominate the properties of the whole

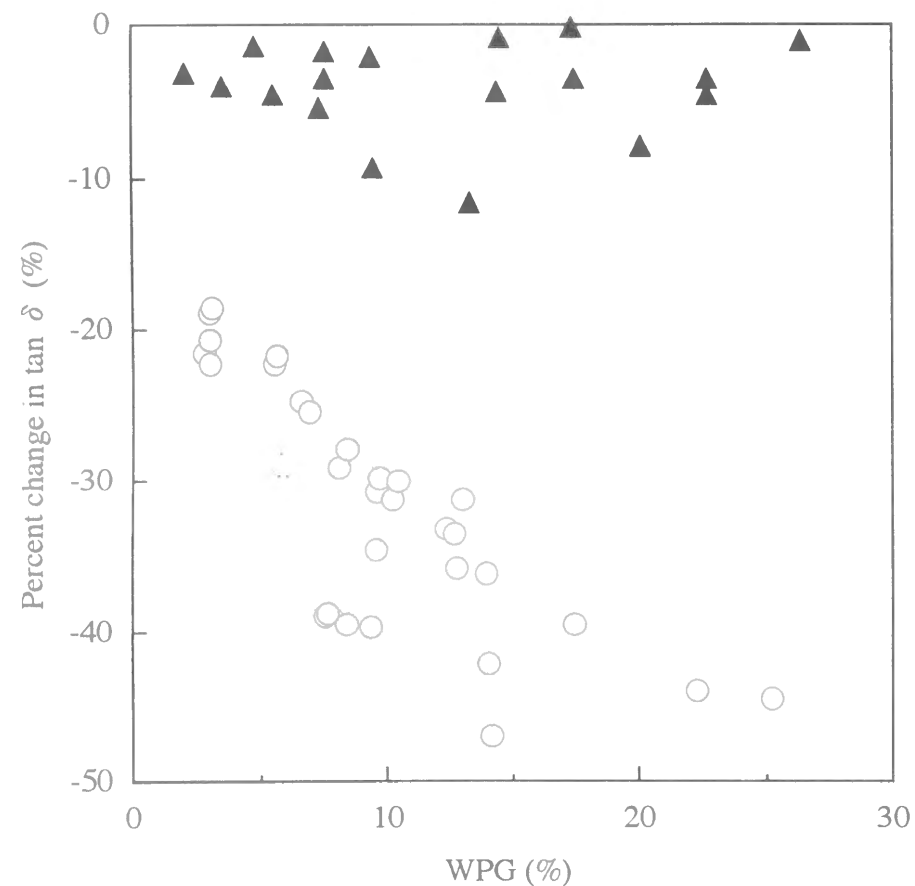


Fig. 3-7. Relationship between weight percent gain (WPG) and percent change in $\tan \delta$. Legends are the same as in Fig. 3-2.

specimen. The large change in $\tan \delta$ for impregnated specimens may also be attributed to the drastic change in the vicinity of the surface. Thus if surface application of extractives could change the vibrational properties, it would be an easier process than impregnation. Moreover it would be easier for high-density wood, such as pernambuco, which is difficult to impregnate. Unfortunately, Young's modulus of the surface-applied specimen decreased, while the $\tan \delta$ hardly did so.

3.3.3 Influences of protosappanin B and hematoxylin on the vibrational properties

It was found that the $\tan \delta$ of spruce wood lowers by the impregnation with extractive components of pernambuco, and that the main components of the extractives are protosappanin B and brazilin. However, it would be premature to conclude that the protosappanin B and brazilin predominantly contribute to the lowering of $\tan \delta$. The effect of the impregnation of these two components should be individually examined. Protosappanin B can be obtained by the separation of pernambuco extractives, whereas brazilin was difficult to prepare sufficient amount. Therefore, commercially available hematoxylin was used for the impregnation in place of brazilin. The chemical structure of brazilin is identical with that of hematoxylin without a hydroxyl group at C₄ (Figs. 2-5 and 3-1), thus the effects of both components on vibrational properties may not differ so largely.

Figure 3-8 shows the relationship between WPG and percent change of $\tan \delta$ after impregnation. The $\tan \delta$ of the specimen impregnated with protosappanin B decreased remarkably as same as that of specimen impregnated with extractives from pernambuco. Hematoxylin also lowered $\tan \delta$ of impregnated specimen though the extent of decrease was less than protosappanin B. Figures 3-9 and 3-10 show the percent changes of E'/γ and E' , respectively. The change of properties of specimen impregnated with protosappanin B and hematoxylin showed almost the

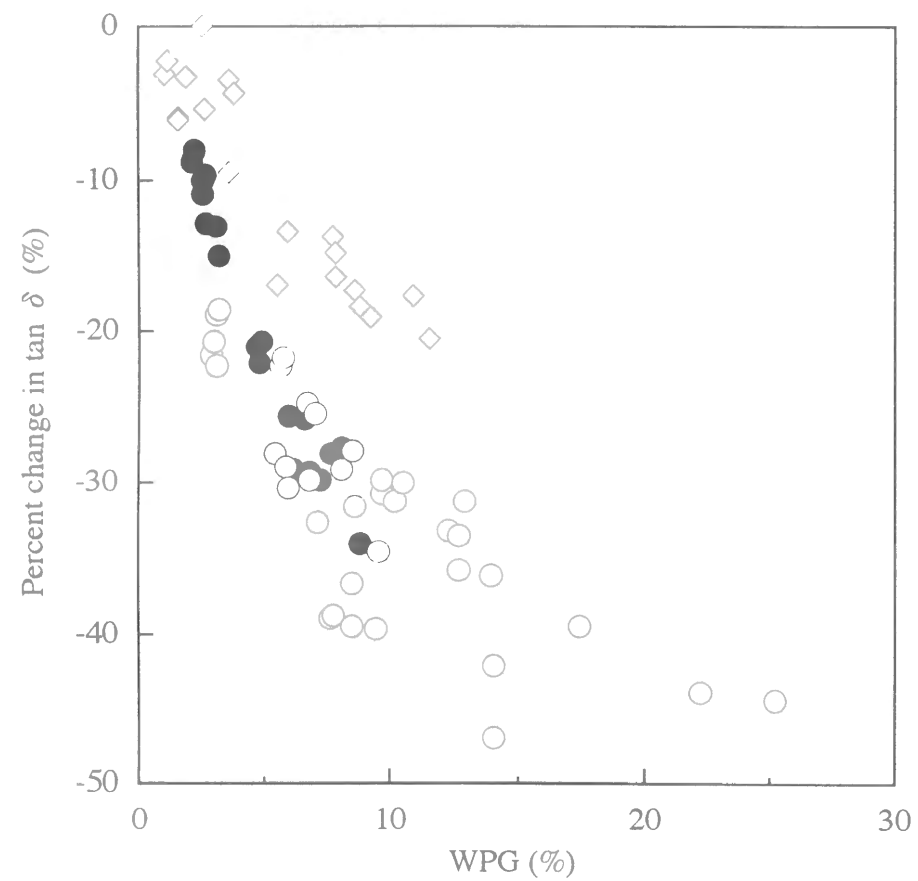


Fig. 3-8. Relationship between weight percent gain (WPG) and percent change in $\tan \delta$ after impregnation under evacuation.

○; Extractives of pernambuco, ●; Protosappanin B,
◇; Hematoxylin.

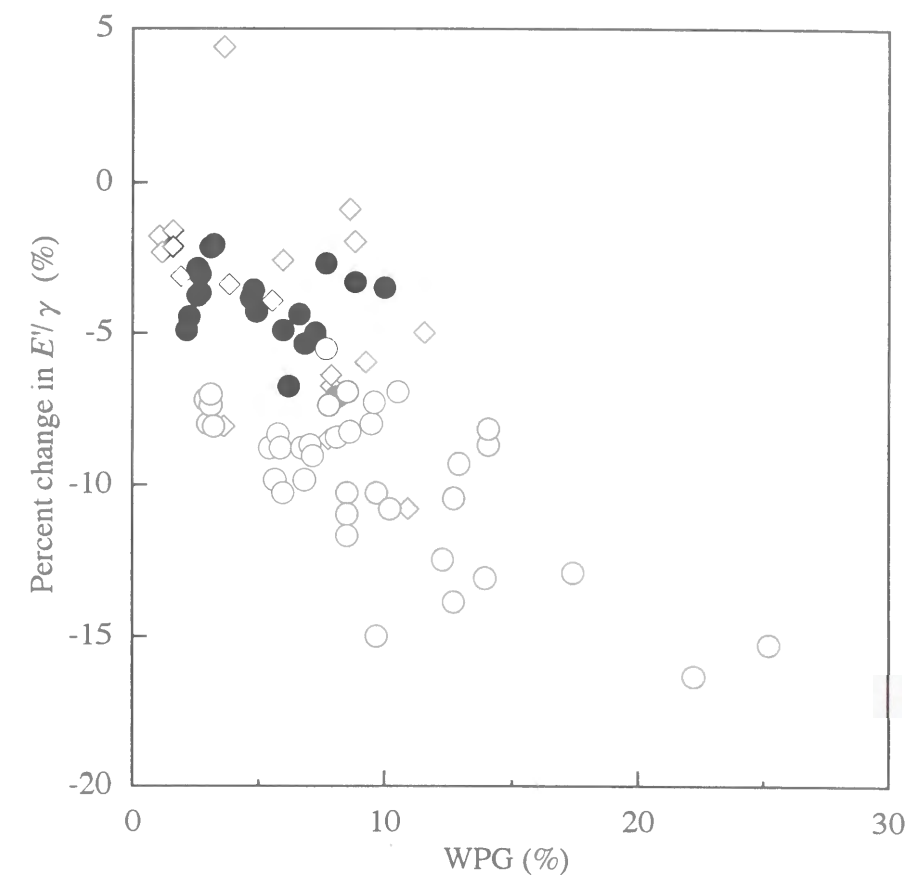


Fig. 3-9. Relationship between weight percent gain (WPG) and percent change of E'/γ after impregnation under evacuation.

Legends are the same as in Fig. 3-8.

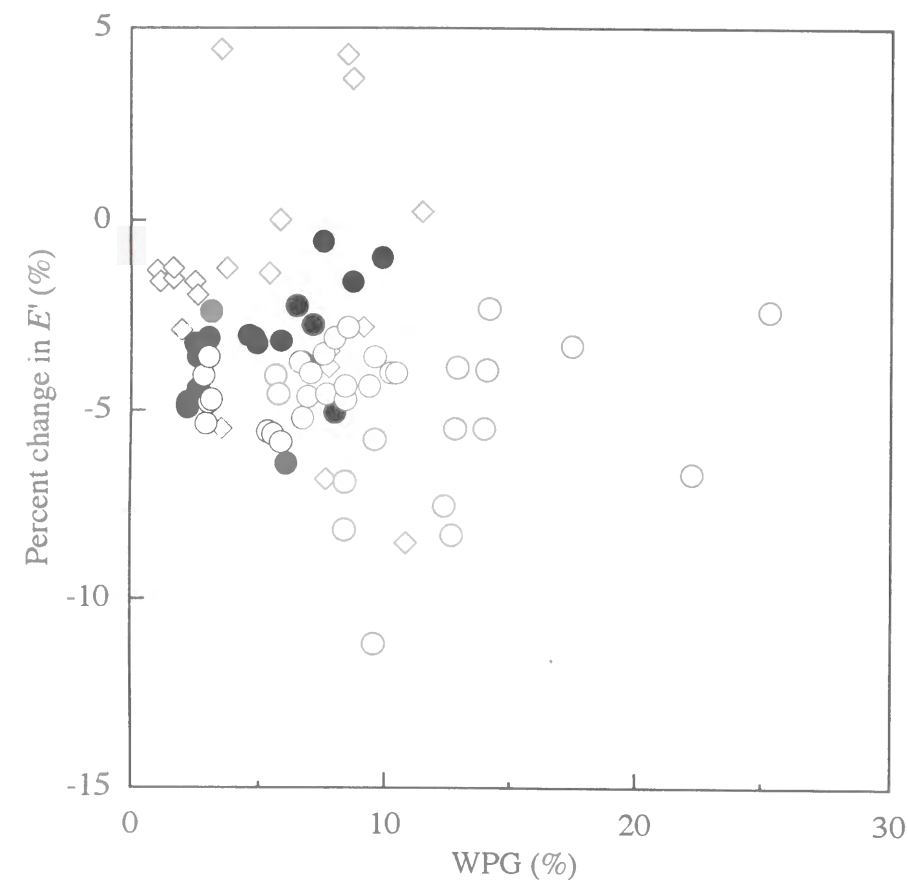


Fig. 3-10. Relationship between weight percent gain (WPG) and percent change in E' after impregnation under evacuation. Legends are the same as in Fig. 3-8.

same tendency as those impregnated with unpurified extractives. From these results, it was cleared that protosappanin B dominantly influences to the change of vibrational properties due to impregnation with extractives of pernambuco.

Protosappanin B has five hydroxyl groups, so it can be proposed that protosappanin B forms hydrogen bonds between neighbouring hydroxyl groups of wood components. On the other hand, it is supposed that brazilin is also one of the components which contribute to decreasing the $\tan \delta$ of wood by impregnation because the impregnation of hematoxylin brought about the extreme decrease of $\tan \delta$.

3.4 Summary

Sitka spruce wood was treated with water-soluble extractive components of pernambuco by impregnation under evacuation and surface application. The changes of vibrational properties were examined. In the case of surface application, the $\tan \delta$ decreased only a small extent, whereas E'/γ decreased with the increase of WPG. On the other hand, the $\tan \delta$ of the impregnated specimens decreased drastically in proportion to the WPG, and the E'/γ decreased only moderately, mainly due to the increase in specific density. Almost all of the extractive components were impregnated in an amorphous region of the cell walls rather than in the lumens. It is proposed that the extractive components formed secondary bonds (such as hydrogen bonds) between matrix substances, resulting in the observed decrease in $\tan \delta$. It was supposed that protosapannin B contributed more greatly than brazilin to the decrease of $\tan \delta$.

Chapter 4 Working Mechanism of Adsorbed Water on the Vibrational Properties of Wood Impregnated with Extractives of Pernambuco

4.1 Introduction

The impregnation with the extractive components into Sitka spruce decreased significantly the $\tan \delta$ of the specimen. Minato *et al.* (1997) and Sakai *et al.* (1998) impregnated catechol, which is a structural unit common in that of protosapannin B and brazilin, and several kinds of substituted phenolic compounds to Sitka spruce wood. They reported that the impregnation with these compounds increases the $\tan \delta$ with increasing WPG independent of their chemical structures. Akitsu *et al.* (1991, 1993) also reported that the $\tan \delta$ of Glehn's spruce (*Picea glehnii*) increased drastically after impregnation with polyethylene glycol and ethylene oxide, which have a dimensional stabilizing effect. Thus, the remarkable decrease of $\tan \delta$ due to impregnation with extractives of pernambuco is a peculiar phenomenon. The reason the extractives of pernambuco lower the $\tan \delta$ is not clear so far.

The $\tan \delta$ of wood varies depending on the moisture content (MC); the $\tan \delta$ of Sitka spruce decreased roughly up to about 6% - 7% MC and then increased with increasing MC (Kollmann *et al.* 1960). In previous chapter, the change of $\tan \delta$ was discussed only under definite conditions (20 °C and 65% R.H.). However, the lowering mechanism of $\tan \delta$ due to impregnation with extractives of pernambuco must be discussed relating it to the MC, because protosapannin B and brazilin have many hydroxyl groups that can absorb the water molecules. Also regarding the vibrational properties, the estimation was limited to the under 1200 Hz range so far, but it is important to determine the vibrational properties changes at a wider frequency range.

In this chapter, the influence of impregnating pernambuco extractive on the moisture adsorption property of the wood specimen is described. The author then measured the frequency dependence of vibrational properties and temperature dependence of $\tan \delta$ at various MCs. Based on the results the mechanism of lowering $\tan \delta$ due to impregnation with extractives is discussed comprehensively.

4.2 Materials and Methods

4.2.1 Preparation of water-soluble extractives from pernambuco

Approximately 30 g of water-soluble extractive was obtained by the same procedure described in 3.2.2. A part of the wood meal before and after extraction (weight loss: 13.5%) and the freeze-dried extractives themselves were used to prepare the moisture adsorption isotherms.

4.2.2 Preparation of moisture adsorption isotherms

Water-soluble extractives of pernambuco (hereafter referred to as extractives), wood meal of pernambuco before and after extraction (weight loss 13.5%), wood meals of Sitka spruce, and Sitka spruce meals impregnated with extractives were used for the moisture adsorption experiments. About 300 mg of each sample was subjected to the test. The impregnated meals were prepared by dipping the Sitka spruce meals into the aqueous solution of extractives with occasional evacuation. The uptakes of the extractives were 5.9%, 11.5%, and 19.2% depending on the concentration of the dipping solutions. Before the moisture adsorption test, the samples were dried at 60 °C for 24 hours under vacuum and weighed. Moisture adsorption isotherms were obtained over various saturated salt solutions in desiccators at 20 °C. The relative humidity values over the saturated salt solutions were adopted from the table summarized by Yano (1968). The adsorption

equilibrium was attained by conditioning for more than 2 weeks. The equilibrium moisture content (EMC) was calculated on the basis of the oven-dried values after impregnation.

4.2.3 Treatment of spruce wood with extractives

Spruce wood specimens were impregnated with extractives by the method described in 3.2.3(a). The specimens were 150 mm (L) \times 12 mm (R) \times 2 mm (T) for the measurement of frequency dependence of vibrational properties and 75 mm (L) \times 4 mm (R) \times 1 mm (T) for dynamic viscoelastic properties.

4.2.4 Measurement of frequency dependence of vibrational properties

Vibrational properties of impregnated and untreated specimens were measured by the same method described in 1.2.3. The frequency dependencies of vibrational properties were measured at six resonant frequencies by increasing the vibrational mode from the first to sixth. Measurements were carried out in an airtight acrylic box that was kept at 24 ° \pm 2 °C. Relative humidities were adjusted by their respective saturated salt solutions: The relative humidities over the saturated salt solutions of MgCl₂·6H₂O, NaBr, and KNO₃ were estimated as about 33%, 58%, and 94%, respectively (Yano 1968). The specimens were kept for more than 2 weeks at each relative humidity before measurement. Table 4-1 shows the MCs of specimens at each relative humidity. The 0% R.H. was achieved by replacing the box with nitrogen gas and desiccating with P₂O₅. The specimens were previously dried at 60 °C for 2 days under vacuum, cooled in the box, and subjected quickly to the test.

4.2.5 Measurement of temperature dependence of $\tan \delta$

Impregnated and untreated specimens were conditioned at 11%, 33%, 58%,

Table 4-1. Weight gain and moisture content of specimens used for the measurement of frequency dependence of vibrational properties (upper) and dynamic viscoelastic properties (lower).

		Moisture content (%)			
		33% R.H.	58% R.H.	94% R.H.	
Untreated	—	5.7	9.4	16.5	
	—	5.5	9.1	16.1	
	—	5.9	9.5	17.1	
	—	5.5	8.7	15.9	
Impregnated	7.6	5.9	9.4	17.4	
	8.5	5.8	9.3	17.1	
	9.4	5.2	8.7	16.7	
	9.7	5.6	9.0	16.9	
	12.3	5.6	9.0	16.9	
	12.9	5.4	9.0	16.6	
	14.1	5.5	9.0	16.4	
	14.1	5.4	8.8	16.4	
	22.2	5.1	8.6	16.2	

		Moisture content (%)			
		11% R.H.	33% R.H.	58% R.H.	94% R.H.
Untreated	—	3.2	5.8	9.6	18.1
	4.8	3.3	6.1	9.8	18.1
Impregnated	9.6	2.9	5.4	8.5	17.1
	12.8	3.3	5.9	8.7	17.0
	16.4	3.3	5.7	9.4	16.6

and 94% R.Hs. and at 24 ± 2 °C for more than 2 weeks. The saturated salt solutions of LiCl, $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$, NaBr, and KNO_3 were used to attain respective relative humidities. The MCs of specimens are shown in Table 4-1. After conditioning at each relative humidity, dynamic viscoelastic properties were measured by a forced vibrational method where a dynamic viscoelastic measuring apparatus (Orientec Co., Reovibron DDV-25PF) was used. Vibrations of 1, 3.5, 11, 33, and 110 Hz were subjected to the specimens under 7.84 N of tension in the span of 58 mm. The temperature range and increasing rate of the temperature were from -150 ° to 20 °C and 1.0 °C/min, respectively. The change of MC during the measurement was regarded to be negligible. The measurement was repeated after drying over P_2O_5 at 24 ± 2 °C for 2 days under vacuum (about 0.3% MC), and drying at 105 °C for 12 hours under vacuum (regarded as 0% MC).

4.3 Results and Discussion

4.3.1 Analysis of adsorption isotherm

Isotherms for pernambuco before and after water-extraction are illustrated in Fig. 4-1. The EMC increased in whole relative humidity range by extraction. The Hailwood-Horrobin adsorption equation (Hailwood *et al.* 1946) was fitted to the isotherms (Fig. 4-1). With this theory, the whole adsorbed water can be classified as hydrated water (M_h) and dissolved water (M_s), which correspond to the water molecules that constitute the monolayer and multilayer in the BET adsorption equation, respectively. Both M_h and M_s increased after extraction. It is thought that the increase of M_h reflects the increase of moisture adsorbable sites, which were occupied with extractives before extraction. On the other hand, the increase of M_s may result from the spatial increase of the moisture adsorbable area due to the

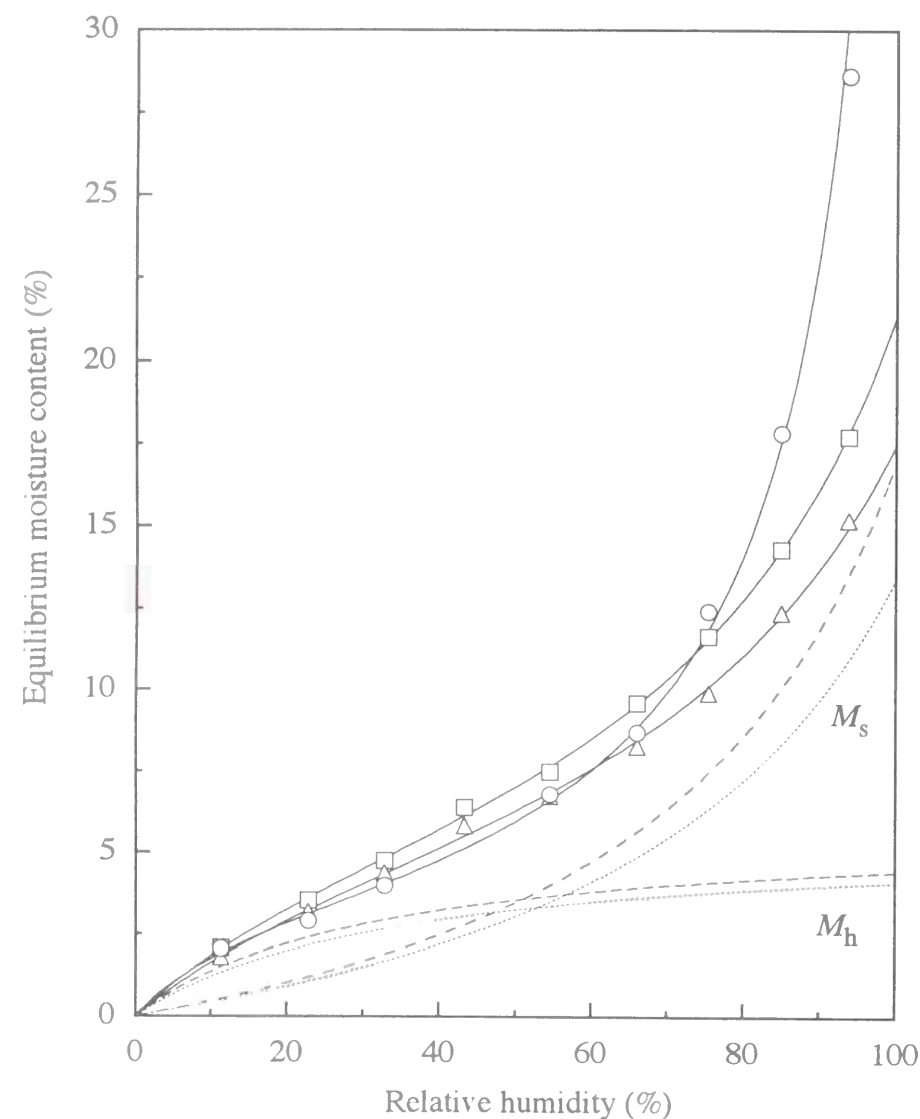


Fig. 4-1. Isotherms for extractives of pernambuco and for pernambuco before and after extraction, and calculated curves for hydrated water (M_h) and dissolved water (M_s) of pernambuco before and after extraction. ○; Extractives of pernambuco, △; Pernambuco before extraction, □; Pernambuco after extraction, ·····; Calculated curves of pernambuco before extraction, - - -; Calculated curves of pernambuco after extraction.

removal of extractives.

The isotherm for extractives themselves showed a steep increase at above 80% R.H. (Fig. 4-1). Obataya *et al.* (1995c) reported that the isotherm for water-soluble extractives of cane, mainly consisting in sugars such as glucose, fructose and sucrose (Obataya *et al.* 1999), showed an abrupt increase at the high relative humidity range. Also for the extractives of pernambuco the steep increase at high relative humidity can probably be attributed to hygroscopic sugars in the extractives. Nevertheless, the lower EMC before extraction results from the fact that the amount of sugars in extractives is not so high that it does not elevate the MC of whole wood.

Figure 4-2 shows the isotherms for extractives in impregnated and untreated Sitka spruce wood. The EMC of impregnated Sitka spruce decreased with increasing WPG. The calculated curves for M_h and M_s showed that both M_h and M_s decreased after impregnation (Fig. 4-3). The decrease of M_h implies a decrease in the water molecules adsorbed directly onto the wood components or extractives; therefore it is thought that one molecule of impregnated component (*e.g.*, protosappanin B or brazilin) occupies many of the sites available for water adsorption. The decrease of M_s is probably due to the decreased space where multilayer adsorption can be performed.

4.3.2 Frequency dependence of vibrational properties

Figure 4-4 shows the dependence of E' and E'/γ on frequency for the impregnated and untreated specimens conditioned at 58% R.H. (MC 8.6% - 9.5%). The E' of the impregnated specimens was almost the same as that of untreated ones over the whole frequency range. On the other hand, the E'/γ of the impregnated specimens was somewhat lower than that of the untreated ones because of the increase of γ . Impregnated specimens conditioned in other relative humidities had

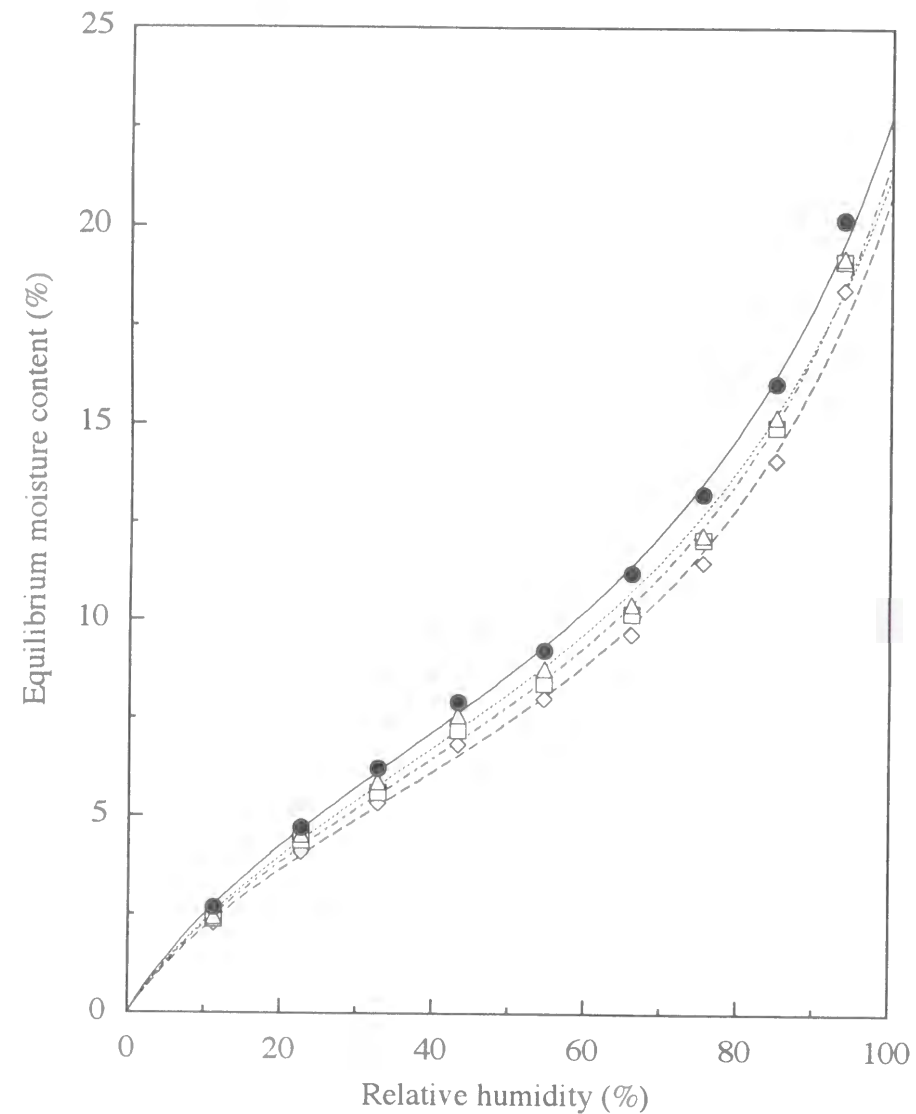


Fig. 4-2. Isotherms for impregnated and untreated spruce wood.
 \triangle ; Impregnated wood (weight percent gain (WPG) is 5.9%),
 \square ; Impregnated wood (WPG is 11.5%),
 \diamond ; Impregnated wood (WPG is 19.2%),
 \bullet ; Untreated wood.

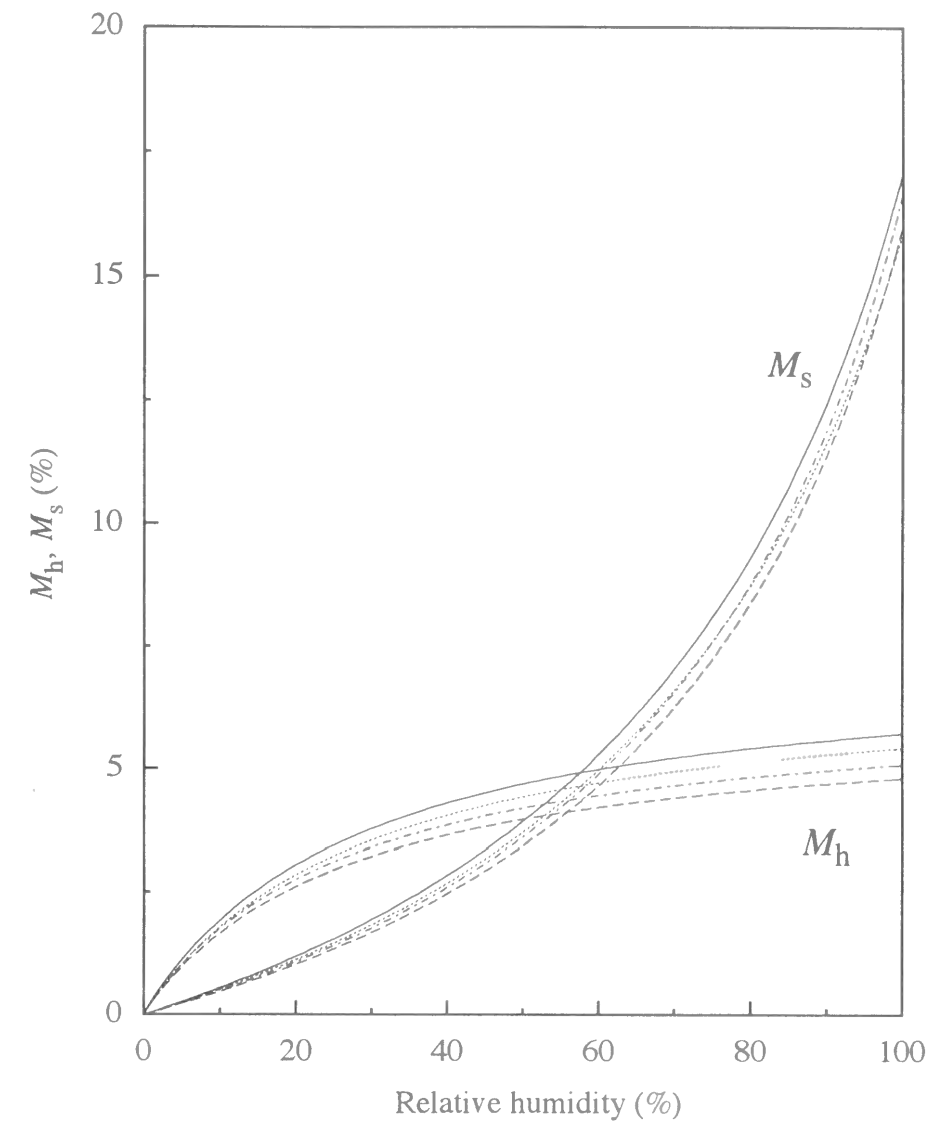


Fig. 4-3. Calculated curves for hydrated water (M_h) and dissolved water (M_s).
 \cdots ; Impregnated wood (WPG is 5.9%),
 $---$; Impregnated wood (WPG is 11.5%),
 $- \cdot -$; Impregnated wood (WPG is 19.2%),
 $---$; Untreated wood.

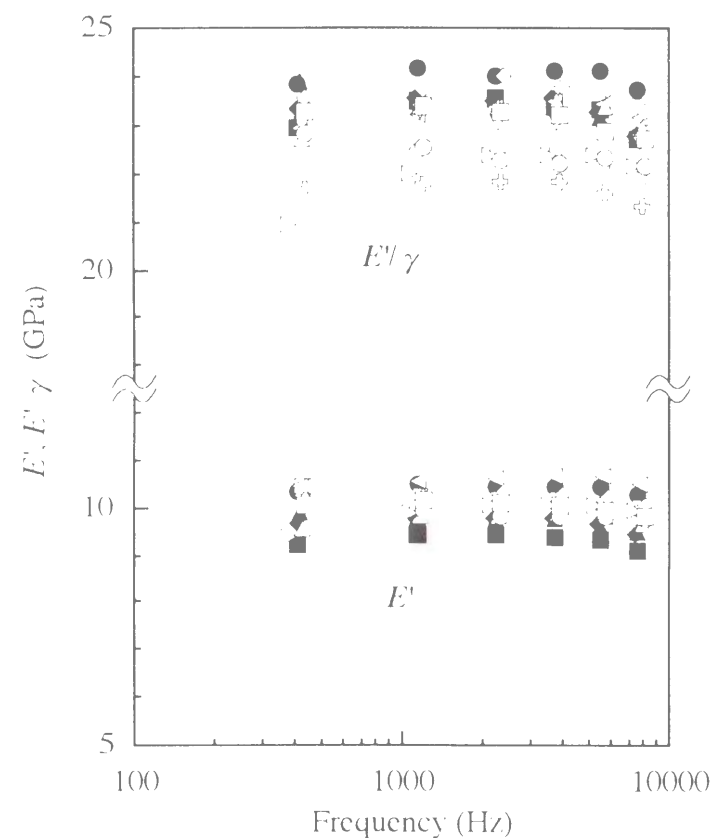


Fig. 4-4. Dependences of E' and E'/γ on frequency for the impregnated and untreated specimens conditioned at 58% R.H.
 ○ □ △ ◇ ; Impregnated wood,
 ■ ◆ ● ▲ ; Untreated wood.

virtually the same E' and somewhat lower E'/γ than those of untreated ones.

Figure 4-5 shows the dependence of $\tan \delta$ on frequency for impregnated and untreated specimens. When the specimens were conditioned at an absolutely dry state, 33% R.H. (MC 5.1% - 5.9%) and 58% R.H. (MC 8.6% - 9.5%), the $\tan \delta$ decreased drastically over the whole frequency range (Fig. 4-5(a)-(c)). The decrease of $\tan \delta$ in the high frequency region was not as extreme. In contrast, when the impregnated specimens were conditioned at 94% R.H. (MC 15.9% - 17.4%), the $\tan \delta$ of the impregnated specimens did not differ from that of untreated ones at around 400 Hz, though the plots were distributed widely (Fig. 4-5(d)). The $\tan \delta$ of the impregnated specimen decreased with increasing frequency and reached a minimum at around 4000 Hz. After that, the $\tan \delta$ increased with increasing frequency and approached that of untreated specimens in the high frequency region. The relation between WPG and $\tan \delta$ was drawn using $\tan \delta$ at 500, 4000, and 7000 Hz, which were obtained by smoothing the relation between resonant frequency and $\tan \delta$ of each specimen. The $\tan \delta$ of impregnated specimens conditioned at 58% R.H. decreased with increasing WPG (Fig. 4-6(c)). In contrast, the $\tan \delta$ of impregnated specimens at 94% R.H. increased with increasing WPG (Fig. 4-6(d)). For the specimens conditioned at the absolutely dry condition and 33% R.H., no definite tendencies were observed in the range of 7.6% - 22.2% WPG(Figs. 4-6(a) and (b)).

The influence of extractive impregnation on the $\tan \delta$ varied depending on the ambient humidity. Figure 4-7 shows the relation between MC and $\tan \delta$ at the first vibrational mode. The values for impregnated specimens (WPG 7.6%, 12.3%, 22.2%) and a mean value of untreated specimens are included in Fig. 4-7. This figure shows that the $\tan \delta$ values of impregnated specimens were lower than those of untreated specimens below about 10% MC, whereas the difference between

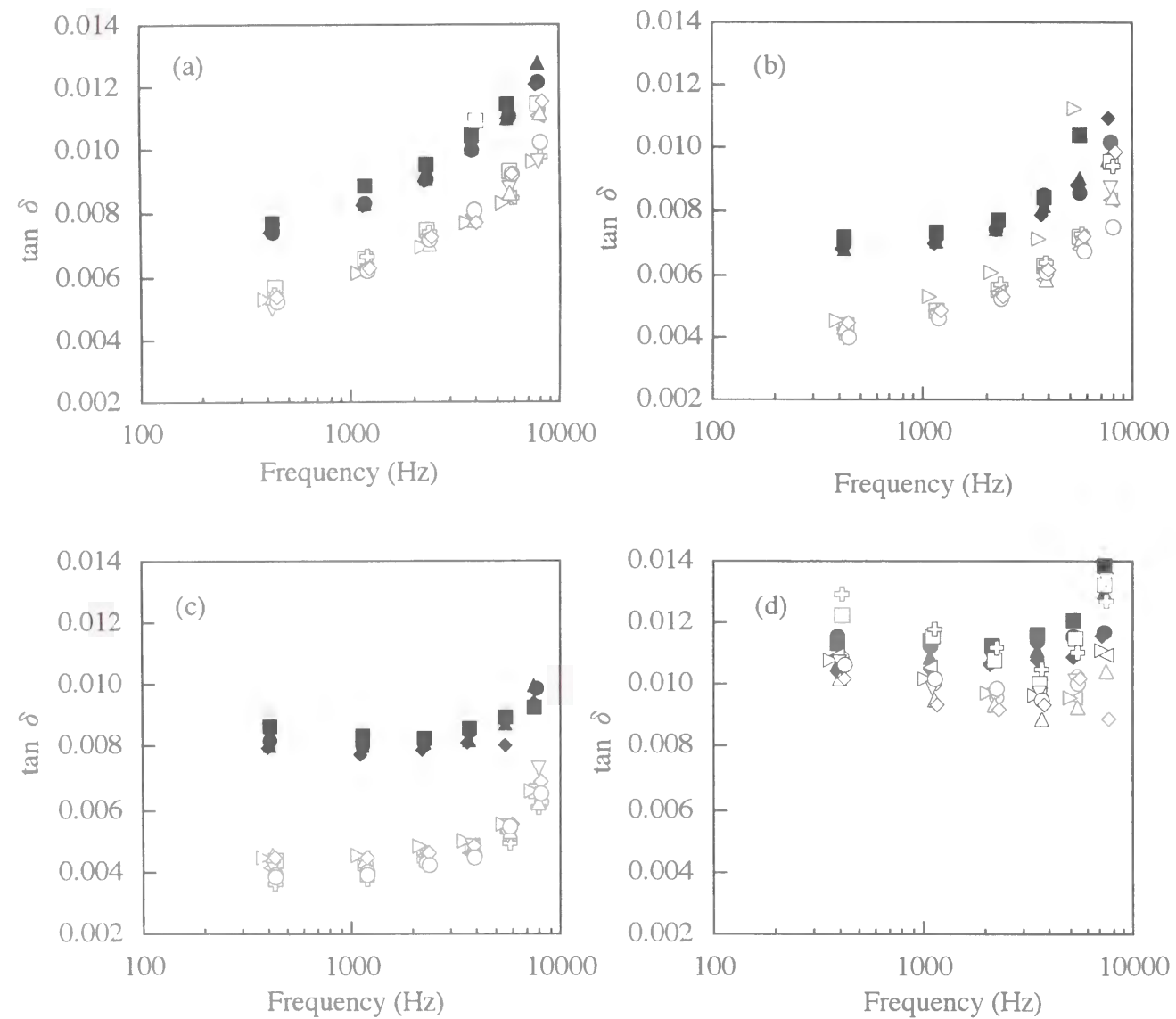


Fig. 4-5. Dependences of $\tan \delta$ on frequency for impregnated and untreated specimens conditioned at absolutely dried state (a), 33% R.H. (b), 58% R.H. (c), and 94% R.H. (d). Legends are the same as in Fig. 4-4.

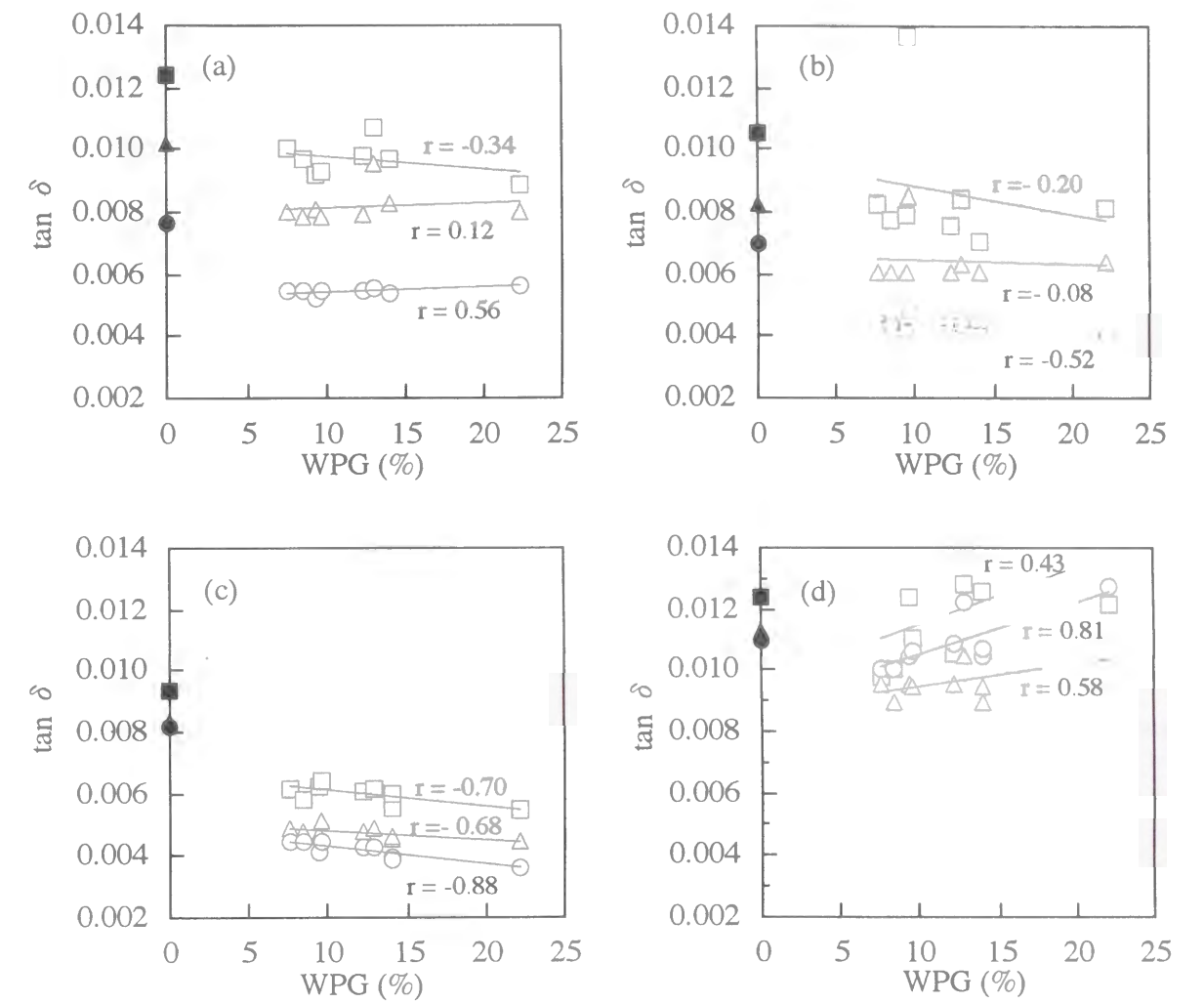


Fig. 4-6. Relation between weight percent gain (WPG) and calculated $\tan \delta$ conditioned at absolutely dried state (a), 33% R.H. (b), 58% R.H. (c), and 94% R.H. (d).
○; Impregnated wood at 500 Hz, ●; Untreated wood at 500 Hz,
△; Impregnated wood at 4000 Hz, ▲; Untreated wood at 4000 Hz,
□; Impregnated wood at 7000 Hz, ■; Untreated wood at 7000 Hz,
r; correlation coefficient.

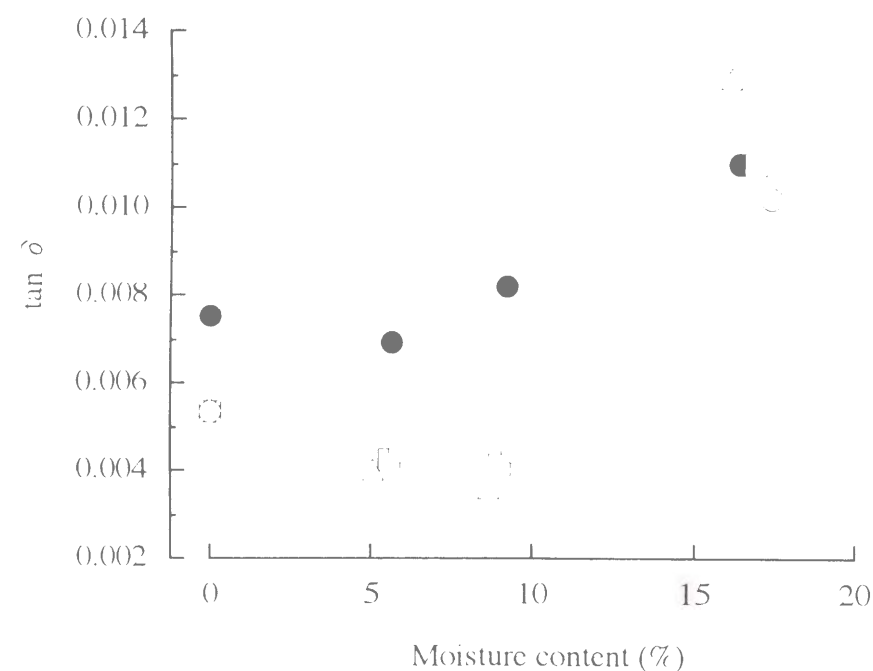


Fig. 4-7. Relation between moisture content and $\tan \delta$.

- ; Impregnated wood (weight percent gain (WPG) is 7.6%),
- ; Impregnated wood (WPG is 12.3%),
- △; Impregnated wood (WPG is 22.2%),
- ; Untreated wood.

them was not significant at around 16% - 17% MC. The $\tan \delta$ of the specimen that has a high WPG seems to be more dependent on the change of MC.

4.3.3 Temperature dependence of $\tan \delta$

The measurement for temperature dependence of viscoelasticity will become one of the useful means to clarify why extractives influence the vibrational properties of wood. Especially, information about the motions of matrix substances or adsorbed water molecules are obtainable by measuring viscoelasticity at low temperature.

Figure 4-8 shows the temperature dependence of $\tan \delta$ at 11 Hz for impregnated and untreated specimens. For the specimens conditioned at 58% R.H. (MC 8.5% - 9.8%), the $\tan \delta$ of impregnated specimens differed clearly from that of untreated ones at above -50°C (Fig. 4-8(e)). The impregnated specimens conditioned at 0%, 0.3%, 11%, and 33% R.H. (Figs. 4-8(a)-(d)) also showed greater decrease of $\tan \delta$ than untreated ones around 0° - 20°C . In contrast, the impregnated specimens conditioned at 94% R.H. (MC 16.6% - 18.1%) had a lower $\tan \delta$ than untreated ones at above -75°C (Fig. 4-8(f)), but the $\tan \delta$ of impregnated specimens increased with increasing temperature at above 25°C , though the $\tan \delta$ of untreated specimens was virtually constant at the temperature range of -75° to 20°C .

When the MC of the impregnated specimen is low, the $\tan \delta$ decreased over a wide temperature range. This phenomenon corresponds to the decrease of $\tan \delta$ determined over a wide frequency range at room temperature (Figs. 4-5(a)-(c)). Meanwhile, when MC is high, the $\tan \delta$ of the impregnated specimens increased with increasing temperature at above -25°C . This corresponds to the increase of $\tan \delta$ determined in the low-frequency range at room temperature (Fig. 4-5(d)).

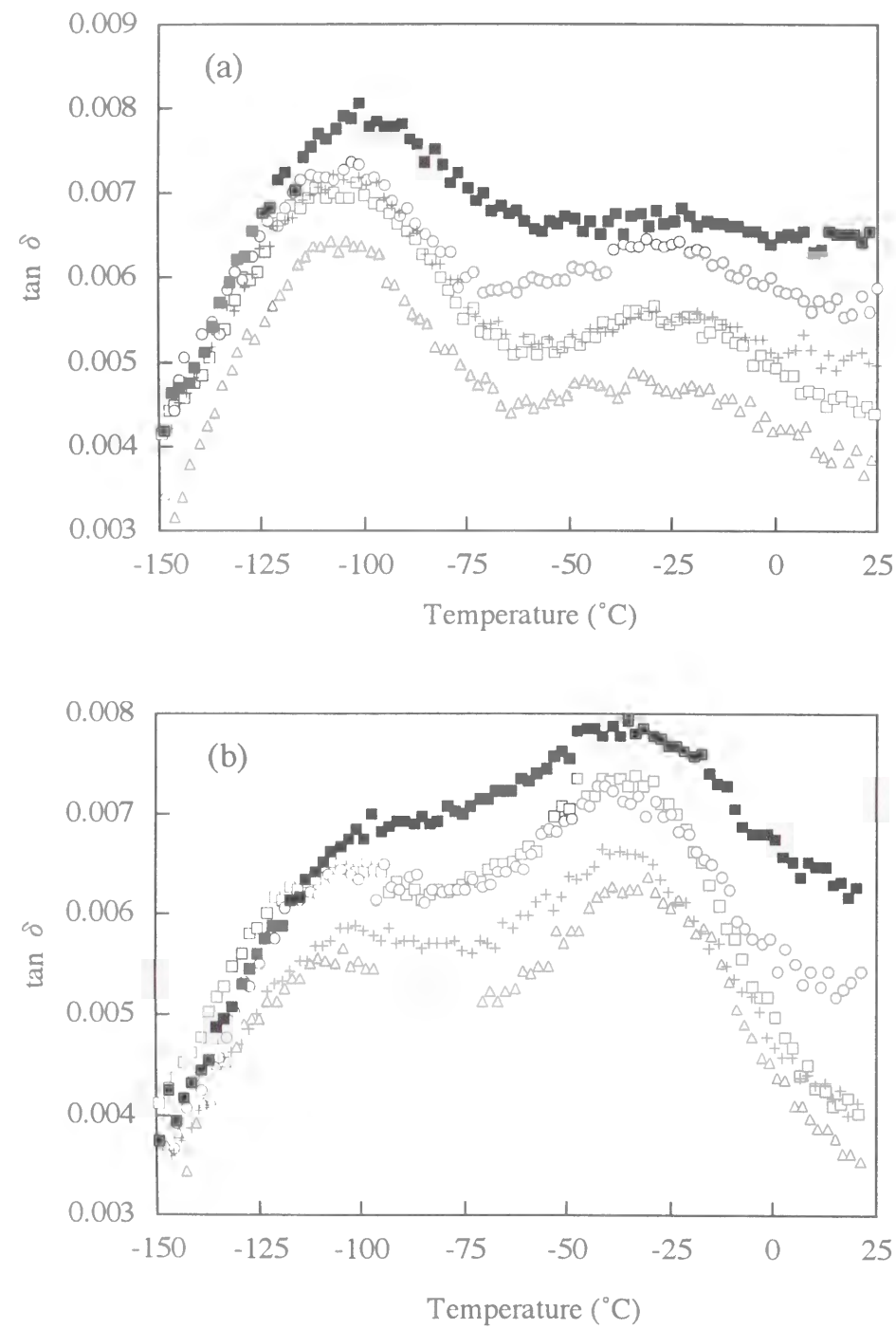


Fig. 4-8. Temperature dependence of $\tan \delta$. (a); 0% R.H., (b); 0.3% R.H.

- +; Impregnated wood (weight percent gain (WPG) is 4.8%),
- ; Impregnated wood (WPG is 9.7%),
- ; Impregnated wood (WPG is 12.8%),
- △; Impregnated wood (WPG is 16.4%),
- ; Untreated wood.

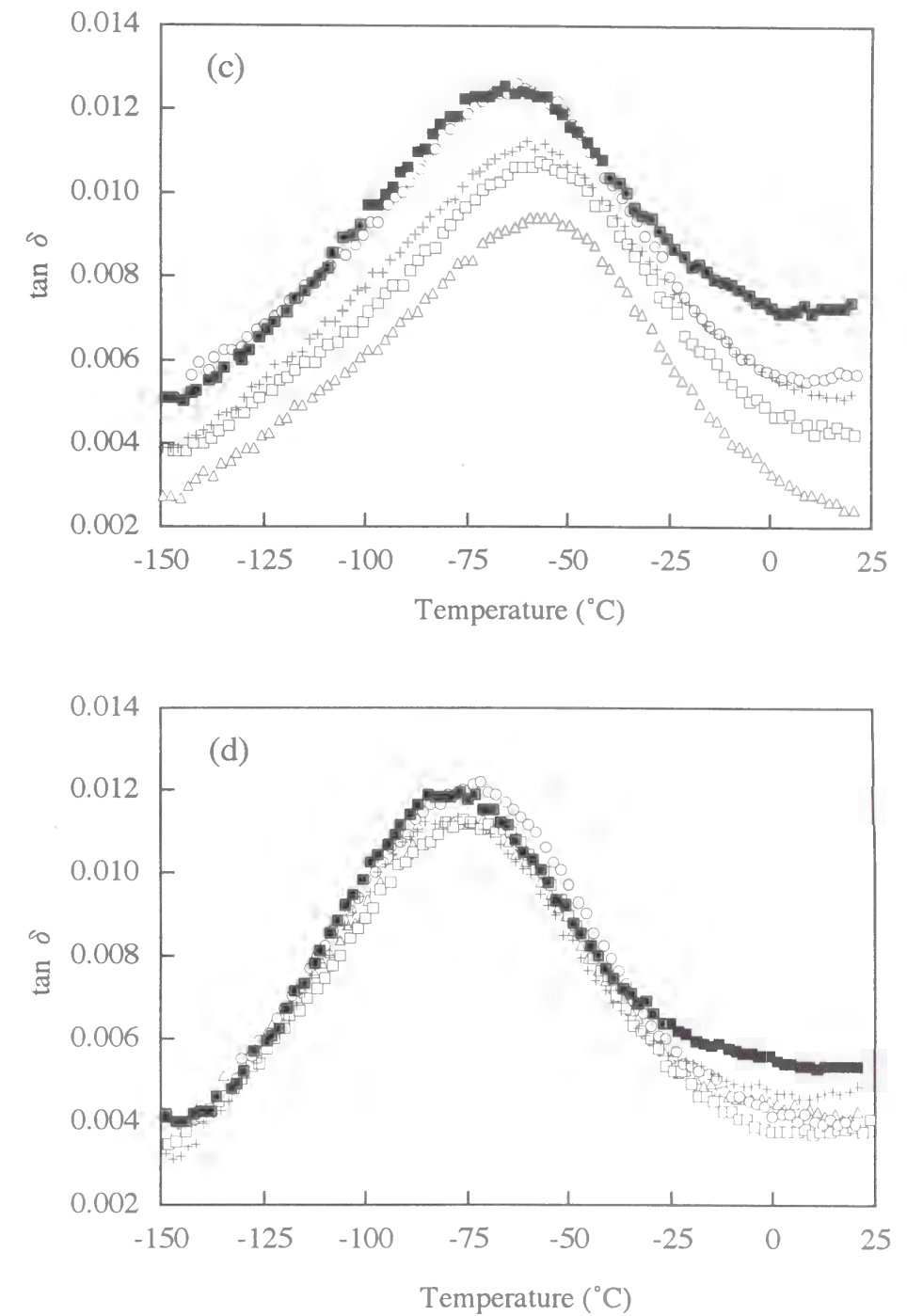


Fig. 4-8. Temperature dependence of $\tan \delta$ (continued).

(c); 11% R.H., (d); 33% R.H.

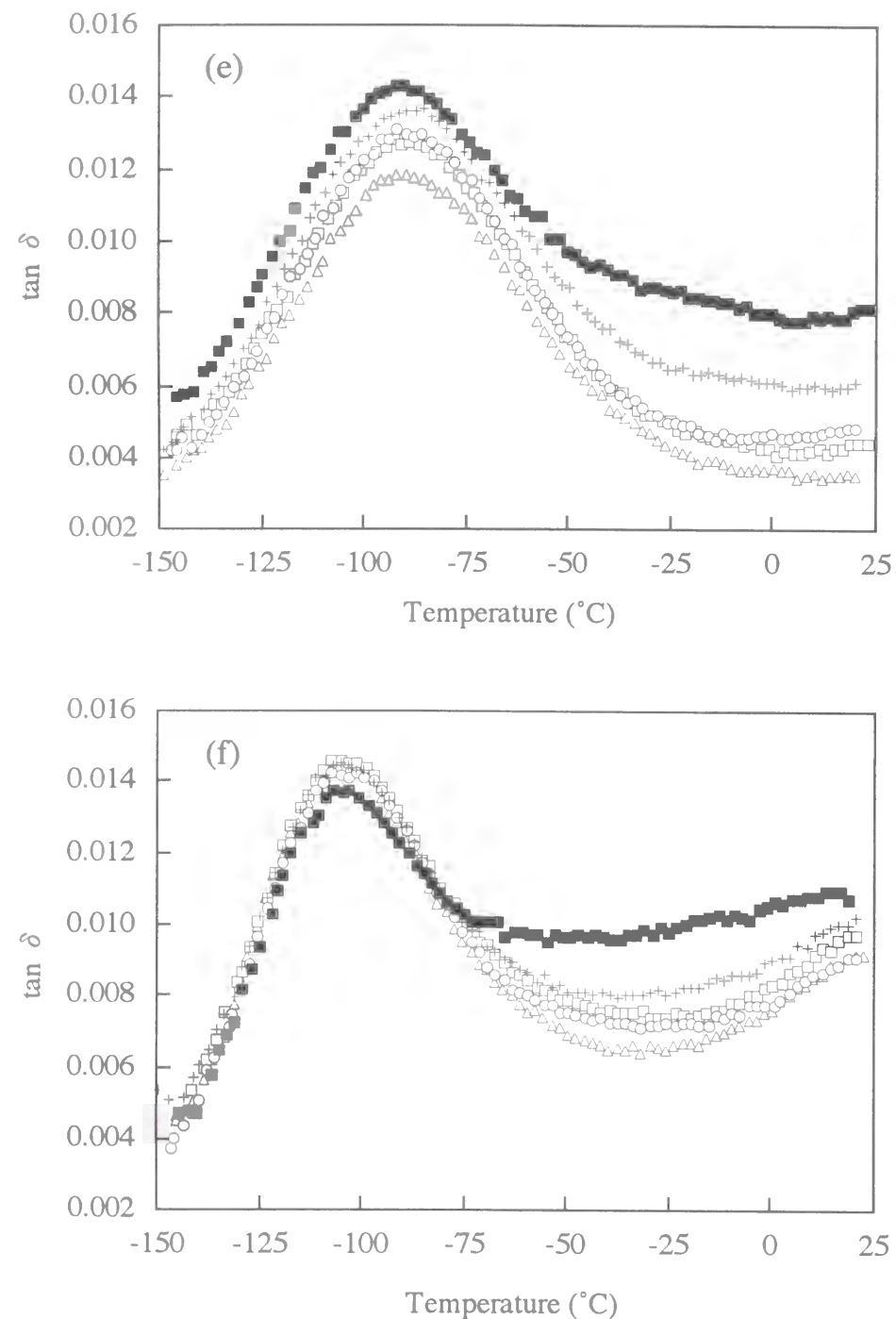


Fig. 4-8. Temperature dependence of $\tan \delta$ (continued).
(e); 58% R.H., (f); 94% R.H.

Figures 4-5(d) and 4-8(f) suggest that the relaxation process exists at a lower frequency or higher temperature range than the measured one. The glass transition temperature of matrix substances, such as lignin, exists at around 100 °C in a humid state (Going 1963). However, the glass transition temperature is lowered by addition of formamide (Sadoh 1981). Therefore, it is speculated that at high MC the impregnated extractives behave as a plasticizer together with adsorbed water molecules; as the result, the glass transition temperature falls and the $\tan \delta$ increases above -25 °C.

The peak of $\tan \delta$ found in the temperature range of this study is considered a mechanical relaxation process of adsorbed water molecules (Obataya *et al.* 1996). This peak is called α relaxation process. It is thought that the change of α relaxation caused by impregnation with extractives reflects the change of mobility of adsorbed water molecules or matrix substances concerned with adsorbed water. The peak temperature (T_α) and the apparent activation energy (ΔE) of α relaxation process were plotted against the MC in Fig. 4-9. The ΔE was calculated as follows:

$$\Delta E = -2.303R \frac{d \log f}{d (1/T_\alpha)} \quad (\text{kJ/mol})$$

where R is the gas constant, and f is the frequency (Hz). Except for specimens with low WPG, ΔE of impregnated specimen was generally higher than those of untreated ones at around 5% - 6% MC (Fig. 4-9(b)). Therefore, it is thought that the mobility of adsorbed water molecules or matrix substances related to adsorbed water is restrained until a moderately high MC. The differences of T_α and ΔE between impregnated specimens and untreated ones were not observed in the high MC range.

From the above mentioned results, we propose the following mechanism for

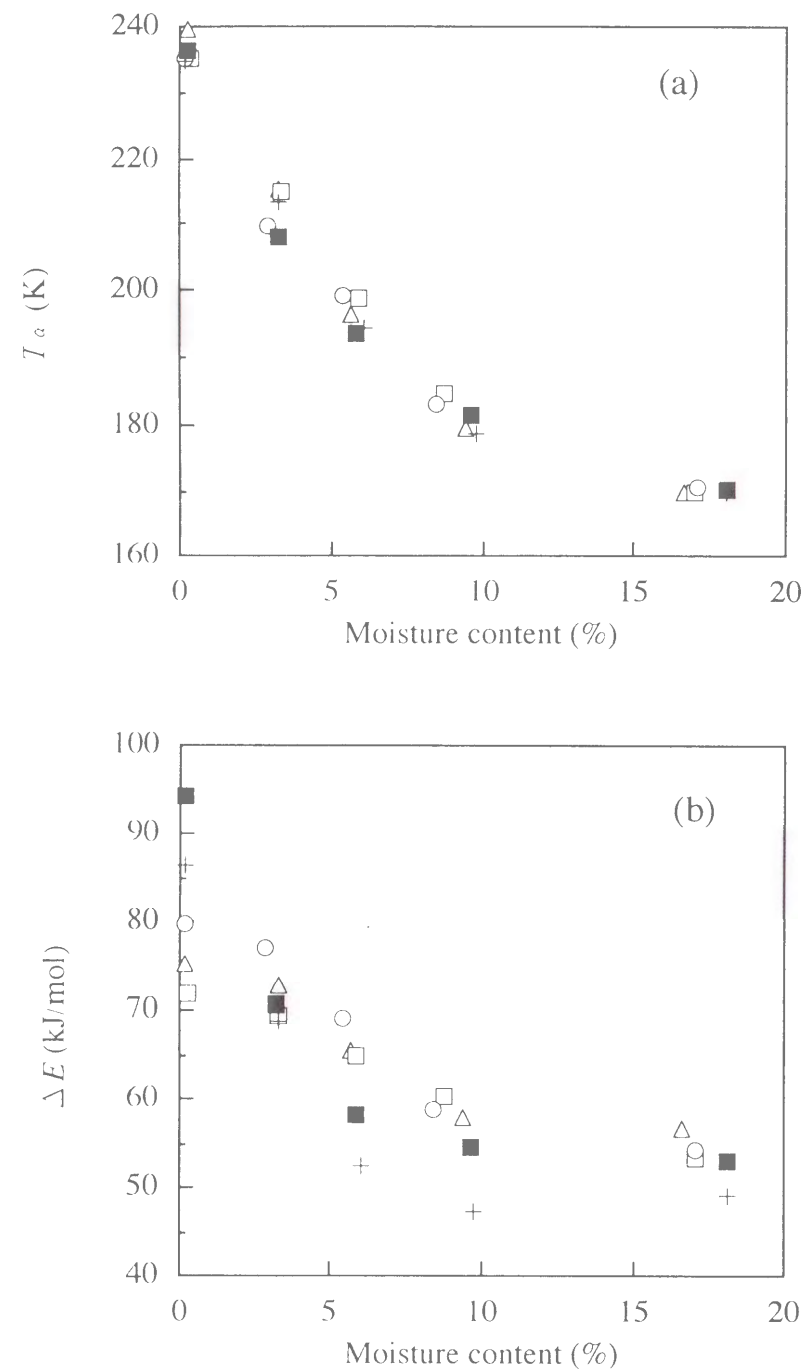


Fig. 4-9. Peak temperature T_α (a) and the apparent activation energy ΔE (b) of α relaxation process plotted against the moisture content. Legends are the same as in Fig. 4-8.

the change of $\tan \delta$ by extractive impregnation. At extremely low MC, the main components of extractives, such as protosapannin B and brazilin, form direct hydrogen bonds with wood components. One molecule of extractive component may form several crosslinkages with wood components, which restrains slippage between molecules or microfibrils. It is also plausible that the rigid structures of protosapannin B and brazilin cause the decreased $\tan \delta$. At moderately high MC, the functional groups of extractives that are apart from the attractive sites of the wood components can also take part in hydrogen bonding through the water molecule, which decreases the $\tan \delta$ even more. At high MC, however, direct hydrogen bonding between the extractive molecule and the wood component becomes impossible because of the existence of an excessive amount of water molecules. As the result, some extractives act as plasticizers and cannot restrain the slippage between molecules or microfibrils. This leads to the increased $\tan \delta$ at high MC.

4.4 Summary

The impregnation of extractives obtained from pernambuco into the Sitka spruce wood changed the $\tan \delta$ differently depending on the MC range. With low to moderate MC, the $\tan \delta$ of impregnated wood decreased probably because of the formation of direct hydrogen bonds between extractive molecules and wood components. With high MC, the decreasing effect of $\tan \delta$ was almost lost. In particular, the fully impregnated specimens showed rather higher $\tan \delta$ than the untreated ones. It is thought that the existence of a large amount of water molecules cleaves the direct hydrogen bonds between the extractive and the wood component, and some extractives behaved as plasticizers.

Conclusions

Generally, violin bow is made from pernambuco (*Guilandina echinata* Spreng. syn *Caesalpinia echinata* Lam.) which is a kind of legminosae growing in Brazil. The heartwood of pernambuco contains the large amount of extractives, which were once used as a dyestuff. Since the latter half of the 18th century, pernambuco is used as the most profitable materials for violin bow. However, there are no reports which prove scientifically why pernambuco is suitable for the bow.

In Chapter 1, pernambuco was compared with alternative wood species from some physical and mechanical aspects and the reasons why it is suitable for bows were discussed. It was found that a low value of loss tangent ($\tan \delta$) was helpful for bow material, as the $\tan \delta$ of pernambuco was much lower than that of the other wood species. This characteristic coincides with the function of a bow, and thus may be necessary for the bow. On the other hand, the most suitable Young's modulus could not be clarified, but the lower limit of Young's modulus needed for the bow must exist. The presence of extractives effects the thermal softening of wood material, but ease of handling and permanent retention of form are not particularly superior for pernambuco. The shearing strength and indentation hardness of pernambuco were higher than that of the other wood species at the same level of specific gravity. High shearing strength and hardness seem to be effective for preventing damage to the bow, but they would not be an inevitable property for the bow.

A peculiarly low $\tan \delta$ of pernambuco seemed to be related closely with the large amount of extractives contained, so the pernambuco was extracted with water and change of $\tan \delta$ was examined (Chapter 2). As a result, the $\tan \delta$ of pernambuco increased accompanying with the elution of extractives. The main components of the extractives were identified to be protosapannin B and brazilin by

structural analysis. In particular, protosappanin B occupied about 40% of extractives of pernambuco.

From these results, it was speculated that the extractive components collected from the heartwood of pernambuco lower the $\tan \delta$ by the impregnation. In Chapter 3, Sitka spruce (*Picea sitchensis* Carr.) was treated with water-soluble extractive components of pernambuco by two different methods: impregnation under evacuation and surface application. The $\tan \delta$ of the impregnated specimen decreased, up to nearly a half of its original value, with increasing weight percent gain (WPG). It was obvious that extractive components were impregnated into amorphous region of cell walls rather than the lumens. The surface application of the extractive components, on the other hand, hardly brought about the desirable change in the vibrational properties. It was found that protosappanin B made a great contribution to the decrease of $\tan \delta$.

In Chapter 4, the lowering mechanism of $\tan \delta$ by the impregnation with extractives was examined from the aspect of the adsorbed water. Based on these results, it was supposed that the decrease in $\tan \delta$ resulted in the formation of secondary bonds between wood components and extractives. Protosappanin B and brazilin have several hydroxyl groups, so they may form hydrogen bonds between neighbouring hydroxyl groups of wood components. The $\tan \delta$ of impregnated wood decreased at low relative humidity because of the formation of hydrogen bond between impregnated extractives and wood components directly and/or indirectly through water molecule. At higher relative humidity, however, the direct hydrogen bonds are disturbed by the existence of a large number of water molecules, and some extractives act as a plasticizer.

In the course of the study on the aptitude of pernambuco as the violin bow, it was found that the extractives of pernambuco decrease the $\tan \delta$ of wood drastically. Though the quality enhancement of bow material is not promising, it is

interesting to apply the pernambuco extractives or relating compounds to the wood substances for acoustic instruments.

Acknowledgements

The author wishes to express his sincere thanks to Professor Fumiaki Nakatsubo, Division of Forest and Biomaterials Science, Graduate School of Agriculture, Kyoto University, for his discussion and suggestion throughout the course of this study.

The author is indebted to Associate Professor Dr. Kazuya Minato, Division of Forest and Biomaterials Science, Graduate School of Agriculture, Kyoto University, for his unfailing guidance and invaluable suggestions.

Appropriate criticism and suggestion of Professor Dr. Minoru Masuda, Division of Forest and Biomaterials Science, Graduate School of Agriculture, Kyoto University, and continuing encouragement and critical reading of the manuscript of Professor Dr. Misato Norimoto, Wood Research Institute, Kyoto University, are greatly acknowledged.

The author is also indebted to Associate Professor Dr. Toshiaki Umezawa, Wood Research Institute, Kyoto University, Associate Professor Dr. Keiji Takabe, Division of Forest and Biomaterials Science, Graduate School of Agriculture, Kyoto University, Dr. Eiichi Obataya, Institute of Agricultural and Forestry Engineering, University of Tsukuba, for their experimental supports.

The author is grateful to Mr. Kohji Sugito, Sugito Gakkyusha & Company, and to Dr. Yoshikazu Yazaki, CSIRO division of Forest Products, for their supplying of the materials.

It is a great pleasure to acknowledge the hospitality and encouragement of members of Laboratory of the Chemistry of Biomaterials, Division of Forest and Biomaterials Science, Graduate School of Agriculture, Kyoto University.

References

Akitsu, H., M. Norimoto and T. Morooka. 1991. Vibrational properties of chemically modified wood. *Mokuzai Gakkaishi* **37**(7), 590-597.

Akitsu, H., M. Norimoto, T. Morooka and R. M. Rowell. 1993. Effect of humidity on vibrational properties of chemically modified wood. *Wood Fiber Sci.* **25**(3), 250-260.

Cave, I. D. 1966. Theory of X-ray measurement of microfibril angle in wood. *Forest Prod. J.* **16**(10), 37-42.

Craig, J. C., A. R. Naik, R. Pratt, E. Johnson and N. S. Bhacca. 1965. Nuclear magnetic resonance spectra and stereochemistry of the antibacterial principle from *Haematoxylon braziletto*. *J. Org. Chem.* **30**, 1573-1576.

Fukada, E. 1951. The vibrational properties of woods used for the musical instruments. *J. Acoust. Soc. Jpn.* **7**(2), 49-54.

Gilbody, A. W., W. H. Perkin and T. Yates. 1901. Brazilin and Haematoxylin. Part I. *J. Chem. Soc.* **79**, 1396-1411.

Goring, D. A. I. 1963. Thermal softening of lignin, hemicellulose and cellulose. *Pulp Paper Mag. Can.* **64**(12), T517-527.

Hailwood, A. J., S. Horrobin. 1946. Absorption of water by polymers: Analysis in terms of a simple model. *Trans. Farad. Soc.* **42B**, 84-92.

Hearmon, R. F. S. 1966. Theory of the vibration testing of wood. *Forest Prod. J.* **16**(8), 29-40.

Imaizumi, K. 1992. In: The Dictionary of Musical Instrument-Bow (in Japanese), Ed. by K. Naito, Tokyo Ongakusha, Tokyo, pp. 95-97, pp.124-125, pp.13-21.

Kitahara, K. 1966. In: Wood physics (in Japanese), Ed. by T. Morikita, Morikawa Shuppan, Tokyo, pp.113-117.

Kollmann, F. and H. Krech. 1960. Dynamic measurement of damping capacity and elastic properties of wood. *Holz Roh- Werkstoff* **18**, 41-54.

Meinel, H. 1957. Regarding the sound quality of violins and scientific basis for violin construction. *J. Acoust. Soc. Am.* **29**(7), 817-822.

Minato, K., K. Sakai, M. Matsunaga and F. Nakatsubo. 1997. The vibrational properties of wood impregnated with extractives of some species of Leguminosae. *Mokuzai Gakkaishi* **43**(12), 1035-1037.

Nagai, M. and S. Nagumo. 1986. Protosappanin B, a new dibenzoxocin derivative from sappan lignum. *Heterocycles* **24**(3), 601-605.

Narayanamurti, D. 1957. The role of extractives in wood. *Holz Roh- Werkstoff* **15**, 370-380.

Norimoto, M. 1982. Structure and properties of wood used for musical instruments I. On the selection of wood used for piano soundboards. *Mokuzai Gakkaishi* **28**(7), 407-413.

Norimoto, M., T. Ono and Y. Watanabe. 1984. Selection of wood used for piano soundboards. *J. Soc. Rheol. Jpn.* **12**(3), 115-119.

Norimoto M, Tanaka F, Ohgama T, Ikimune R. 1986. Specific dynamic Young's modulus and internal friction of wood in the longitudinal direction. *Wood Res. Tech. Notes* **22**, 53-65.

Obataya, E. and M. Norimoto. 1995a. Acoustic properties of cane (*Arundo donax* L.) used for reeds of woodwind instruments I. The relationships between vibrational properties and moisture contents of cane. *Mokuzai Gakkaishi* **41**(3), 289-292.

Obataya, E. and M. Norimoto. 1995b. Acoustic properties of cane (*Arundo donax* L.) used for reeds of woodwind instruments II. Analysis of vibrational properties by a viscoelastic model. *Mokuzai Gakkaishi* **41**(5), 449-453.

Obataya, E. and M. Norimoto. 1995c. The water sorption isotherms of Cane (*Arundo donax* L.) used for reeds of woodwind instruments. *Mokuzai Gakkaishi* **41**(12), 1079-1085.

Obataya, E., M. Yokoyama and M. Norimoto. 1996. Mechanical and dielectric

relaxations of wood in a low temperature range I: Relaxations due to methylol groups and adsorbed water. *Mokuzai Gakkaishi* **42**(3), 243-249.

Obataya, E., T. Umezawa, F. Nakatsubo and M. Norimoto. 1999. The effect of water soluble extractives on the acoustic properties of reed (*Arundo donax* L.). *Holzforschung* **53**(1), 63-67.

Ono T. and M. Norimoto. 1983. Study on Young's modulus and internal friction of wood in relation to the evaluation of wood for musical instruments. *Jpn. J. Appl. Phys.* **22**(4), 611-614.

Perkin, W. H., J. N. Ray and R. Robinson. 1928. Experiments on the synthesis of brazilin and haematoxylin and their derivatives. Part III. *J. Chem. Soc.* 1504-1513.

Sadoh, T. 1981. Viscoelastic properties of wood in swelling systems. *Wood Sci. Technol.* **15**, 57-66.

Sakai, K., M. Matsunaga, K. Minato and F. Nakatsubo. 1999. Effects of impregnation of simple phenolic and natural polycyclic compounds on physical properties of wood. *J. Wood Sci.* **45**(3), 227-232.

Tanaka, C., T. Nakao and A. Takahashi. 1987. Acoustical property of wood I. Impact sound analysis of wood. *Mokuzai Gakkaishi* **33**(10), 811-817.

Yamamoto, H., T. Okuyama and M. Yoshida. 1993. Methods of determining the mean microfibril angle of wood over a wide range by the improved Cave's method. *Mokuzai Gakkaishi* **39**(4), 375-381.

Yano, H., T. Yamada and K. Minato. 1986. Change in acoustical properties of sitka spruce due to reaction with formaldehyde. *Mokuzai Gakkaishi* **32**(12), 984-989.

Yano, H., K. Oonishi and J. Mukudai. 1990. Acoustic properties of wood for the top plate of guitar. *J. Soc. Mater. Sci. Jpn.* **39**(444), 1207-1212.

Yano, H., I. Matsuoka and J. Mukudai. 1992. Acoustic properties of wood for violins. *Mokuzai Gakkaishi* **38**(2), 122-127.

Yano, H. 1994. The changes in the acoustic properties of Western red cedar due to methanol extraction. *Holzforschung* **48**(6), 491-495.

Yano, Y. 1968. In: Handbook for material and water (in Japanese), Ed. by Kobunshi Gakkai, Kyoritsu Shuppan, Tokyo, pp. 240-264.

Yazaki, Y., P. J. Collins and B. McCombe. 1994. Variations in hot water extractives content and density of commercial wood veneers from blackbutt (*Eucalyptus pilularis*). *Holzforschung* **48**(Suppl.), 107-111.

List of Publications

The present study has been reported in the following papers.

- 1) Sugiyama, M., M. Matsunaga, K. Minato and M. Norimoto. 1994. Physical and mechanical properties of pernambuco (*Guilandina echinata* Spreng) used for violin bows (in Japanese). *Mokuzai Gakkaishi* **40**(9), 905-910. [Chapters 1 and 2]
- 2) Matsunaga, M., M. Sugiyama, K. Minato and M. Norimoto. 1996. Physical and mechanical properties required for violin bow materials. *Holzforschung* **50**(6), 511-517. [Chapters 1 and 2]
- 3) Matsunaga, M. and K. Minato. 1998. Physical and mechanical properties required for violin bow materials II: Comparison of the processing properties and durability between pernambuco and substitutable wood species. *J. Wood Sci.* **44**(2), 142-146. [Chapters 1 and 2]
- 4) Matsunaga, M., K. Minato and F. Nakatsubo. Vibrational property changes of spruce wood by impregnation with water-soluble extractives of pernambuco (*Guilandina echinata* Spreng.). *J. Wood Sci.*, in press. [Chapter 3]
- 5) Matsunaga, M., K. Sakai, H. Kamitakahara, K. Minato and F. Nakatsubo. Vibrational property changes of spruce wood by impregnation with water-soluble extractives of pernambuco (*Guilandina echinata* Spreng.) II: Structural Analysis of Extractive Components. *J. Wood Sci.*, in press. [Chapters 2 and 3]
- 6) Matsunaga, M., E. Obataya, K. Minato and F. Nakatsubo. Working mechanism of adsorbed water on the vibrational properties of wood impregnated with extractives of pernambuco (*Guilandina echinata* Spreng.). *J. Wood Sci.*, in press. [Chapter 4]